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President: J. VAN DER HOEVE
Secretary: M. W. WOERDEMAN

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Chemistry. — *On the sterical conditions in the cyclic acetone-acetals of the ortho-di-phenols.* By J. BÖESEKEN.

(Communicated at the meeting of February 25, 1939.)

After CHR. VAN LOON [1]) had pointed out the significance of the formation of cyclic acetals of polyols for the knowledge of the position in space of the hydroxyl groups, HERMANS [2]) studied very elaborately the equilibria

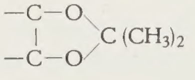
$$\text{Diol} + \text{acetone} \rightleftarrows \text{cyclic acetal} + \text{water}$$

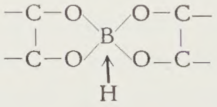
in a number of typical cases.

It was a well-known fact that the increased conductivity of boracic acid produced by polyols is closely connected with the position of these groups in space.

HERMANS now observed that upon the whole the acetone equilibria were situated more to the right according as the influence of the boracic acid increased.

From the boracic acid researches [3]), lastly those of VERMAAS [4]), it became apparent that the increased conductivity is due to the presence of complex mono-diol and didiol boracic acids, the structure of which was long since known, owing to their isolation, analysis and characteristics [2]). These are also cyclic acetals, with this difference that the boron atom takes the place of the carbon atom.





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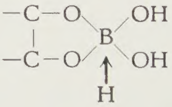

The boron atom is coordinatively tetravalent, which implies that the boro-complexes are strong acids, in contrast with the ordinary cyclic acetals which naturally are neutral.

If the sterical conditions, viz. the distances between the atoms, in the boracic acid compounds may be compared with those of the cyclic acetals, it was to be expected that the increase in conductivity and the position of the acetone equilibrium run parallel and consequently the researches by

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[1]) CHR. V. LOON, Stereochemie der cyclopentaan- en der hydrendeen diolen-1-2. Diss. Delft 1919.

[2]) P. H. HERMANS, Onderzoek naar de ruimtelijke konfiguratie van enkele glykolen. Diss. Delft 1924.

[3]) J. BÖESEKEN, Configuration des polyalcools. Conférence devant la Soc. Chim. de France. 16 juin 1933.

[4]) N. VERMAAS, Rec. trav. Chim., **51**, 67 et 955 (1932).
J. BÖESEKEN and N. VERMAAS, Journ. of Phys. Chem., **35**, 1477 (1931).

HERMANS may be considered as an indication that these distances are indeed of the same order of magnitude.

It was surprising, therefore, that the ortho-di-phenols, which produce a considerable increase in the conductivity of boracic acid and also yielded the first well crystallized boro-complexes, seemed to yield no cyclic acetone compounds.

From an investigation by G. SLOOFF 5) it now appeared that these compounds indeed can be prepared, if the formed water is removed by means of powerful dehydrators, such as P_2O_5 and fuming H_2SO_4.

The possibiliy of formation was thus demonstrated but from the manner of this formation it is yet clear that the acetone *equilibria* have a very unfavourable position, which has been confirmed by G. SLOOFF.

In order to obtain this equilibrium, a small quantity of a powerful catalyzer must be sufficient. If in some way or other the formed water is regularly removed, it is to be expected that the acetal may be obtained in satisfactory yields. This removal of the water may take place by a physical method, viz. by boiling the equilibrial mixture with a neutral liquid, e.g. an aromatic hydrocarbon. The vapour takes the water vapour with it. Subsequently, by condensation of this mixture, the heavier water may be separated from the lighter hydrocarbon and the latter led back into the reaction retort.

This method has been successfully carried out by V. D. SPEK 6) for a great number of aromatic ketone acetals. Particularly for ketones with a fairly high boiling-point it appeared to be very effectual. For acetone itself this method is not suitable, since this is too volatile and consequently is removed with the hydrocarbon. Water is easily dissolved in acetone; consequently no separation of the layers sets in.

From the amount of water caught it may be found how far the reaction has proceeded. The longer duration of the condensations again shows that the acetal equilibria are very unfavourably situated.

SLOOFF (l.c.) has tried to explain this unexpectedly unfavourable position of the hydroxyl groups with regard to the ketone-condensation. He pointed out that the distance between the boron and oxygen atoms may be considerably larger than between C and O, so that the oxygen atoms of the diphenols can be more easily attacked by the boron atom than by the carbon.

V. D. SPEK on the other hand is inclined to think in the first place of the nature of the phenolic hydroxyl group, since, as appears from the behaviour of aldehydes and ketones towards the phenols, only rarely normal acetal formation sets in, but other condensations, e.g. the formation of diphenyl methane derivatives take place.

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5) G. SLOOFF, Cyclische aethers, gevormd door condensatie van pyrocatechol met aldehyden en ketonen. Diss. Delft 1934. See also Rec. trav. Chim. **54**, 995 (1935).

6) J. J. V. D. SPEK, Cyclische acetalen van pyrocatechol. Diss. Delft 1938.

His opinion is supported by the behaviour of naphtalene diol 1.8, which produces an exceedingly strong increase in conductivity and where indeed the hydroxyl groups for the acetal formation (according to the calculations by SLOOFF) would have a more favourable position than those of pyrocatechol, and yet no cyclic acetal can be obtained with acetone. (It may be done with other ketones, though with a bad yield.)

I do not consider this argument of great value, since this diphenol in the presence of powerful catalyzers very easily resinifies and the mobility of the aromatic H-atoms is so great that other condensations than the acetal formation very easily set in.

Since, for the rest, the whole investigation of v. D. SPEK is based upon the equilibrium reaction of the cyclic acetals and the elegant method applied by him often yields excellent results, I am inclined to think that the explanation given by SLOOFF is the correct one. Here we have to consider also that the phenolic hydroxyl groups are kept in their places by the tension in the benzene ring, whereas aliphatic hydroxyl groups by the suppleness of the saturated bonds and, by the unimpeded rotation round the single bond, may far more easily be brought into a position which is more favourable to the acetal formation.

It is, therefore, not only the unfavourable position of the hydroxyl group but also the fact that they are, so to speak, fixed in this position, which drives the acetal equilibrium so far to the left.

Taking into consideration the most probable distances between the atoms, C—C(ar) 1.39; C—O 1.36; B—O 1.53; and assuming that the phenolic hydroxyl groups form angles of 120° with the benzene nucleus, we find a distance between the two O-atoms of 2.75 Å, not sufficient to be attacked by the C-atom, the double C—O distance being 2.72 Å, the double B—O distance 3.06, so quite sufficient.

For the formation of cyclic acetal an inward bend of the phenolic oxygen atoms is necessary and with these stiff groups this requires special energy. In connection with this slight suppleness of the groups linked to the nucleus, it may be expected that in the cyclic acetals the tension will remain.

In order to examine this, Miss DE QUANT determined the heat of combustion 7) of an aromatic and some aliphatic cyclic acetone acetals and of the polyols themselves 8), from which it became indeed apparent that the difference in heat of combustion of acetal and polyol in the aromatic compound exceeded by far the corresponding differences of the aliphatic compounds. The small differences in the highly divergent aliphatic diols are interesting and evidently indicate that in the supple

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7) This was done in the laboratory and under the guidance of Prof. Dr. Ir. P. E. VERKADE at the Nederlandsche Handelshoogeschool at Rotterdam, whom I wish to thank also in this place for his hospitality and assistance.

8) J. H. DE QUANT, De verbrandingswarmte van eenige diolen en hun acetonverbindingen. Diss. Delft 1938.

Acetone acetal of	△ per acetal group
mannitol (tri)	423.5
,, (di)	423.9
,, (mono)	422.2
hydrobenzoine	422.8
cis . hydrendene diol 1 . 2	420.9
cis . tetrahydronaphtalene diol 2 . 3	419.4
cis . phenyl-l-cyclopentane diol 1 . 2	415.0
protocatechuic acid	440.2

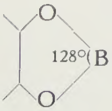
acetal hardly any tensions are present, even in a case where we know with certainty that in the diol the hydroxyl groups have an unfavourable position (hydrobenzoine).

The significance of a slight heat of combustion, as in the case of cis . phenyl-l-cyclopentane diol 1 . 2, cannot be explained without a much larger experimental material.

Although it has to be admitted that the phenolic hydroxyl groups differ also chemically from the alcoholic ones, yet it must be concluded from these researches that the different behaviour of these groups towards boracic acid and acetone is mainly based on sterical grounds. The difference in distance of the coordinatively tetravalent boron atom and the tetravalent carbon atom to oxygen on the one hand and the stiffness of the phenolic hydroxyl group in contrast with the suppleness of the alcoholic group on the other hand offer a satisfactory explanation.

Finally I may draw attention to the fact that the influence of the polyphenols upon the conductivity of boracic acid is not extraordinarily great and only shows considerable differences, as may be seen in the table, if special causes can be expected. Assuming that the angles between the bonds of the nucleus and of the substituent are 120°, we may calculate from the known distances between the atoms that the angle between the boron atom and its affinity directions is about 128°: In connection with the slight suppleness of the aromatic bonds, this is indeed hardly favourable. For 1.8 dihydroxy

Polyphenol	△ mol
pyrocatechol	1012
pyrogallol	1140
hydroxy hydrochinol	644
dinitropyrocatechol	± 31000
dihydroxynaphtalene 1 . 2	2080
,, 2 . 3	3400
,, 1 . 8	134000
protocatechuic acid	2200
gallic acid	900



naphtalene we calculate 104°, which is far more favourable and is reflected in the uncommonly high value for the increase in conductivity. Considering the problem in this light, we must assume that the nitro groups in dinitropyrocatechol bend the hydroxyl groups towards each other. A slight decrease of the two angles of 120° has immediately a strong influence upon the angles of the central boron atom.

Delft, February 1939.

Mathematics. — *Die projektiven Invarianten von vier und fünf Geraden im R_4.* Von R. WEITZENBÖCK.

(Communicated at the meeting of February 25, 1939.)

Bei Geraden $a, \alpha, p, m, \varphi, \ldots$ im vierdimensionalen Raume R_4 ergeben sich auf geometrischem Wege wie folgt die einfachsten projektiven Invarianten: wir verbinden die Geraden a und α zu einem linearen $\mathrm{R}_3\, S'_{12}$, ebenso p und m zu einem Raum S'_{34}. Diese beiden Verbindungsräume schneiden sich in einer Ebene $(S'_{12}\, S'_{34})$. Sie trifft die fünfte Gerade φ, wenn die Invariante

$$\sum_{ik} \varphi_{ik}\, (S'_{12}\, S'_{34})_{ik} = A_{5,\,12,\,34}$$

verschwindet.

Ich beweise im Folgenden, dass sich bei vier und bei fünf Geraden im R_4 jede projektive Invariante durch Invarianten $A_{i,jk,rs}$ der genannten Art ausdrücken lässt. Ueberdies bilden diese Invarianten bei willkürlich vielen Geraden auch eine Rationalbasis für alle projektiven Invarianten.

§ 1. *Allgemeines.*

Wir gehen aus von einer Anzahl willkürlicher Geraden des vierdimensionalen Raumes in allgemeiner Lage mit den Koordinaten

$$a_{ik},\ \alpha_{ik},\ p_{ik},\ m_{ik},\ \varphi_{ik},\ \ldots \qquad (1)$$

und stellen diese Koordinaten dar mit zweifältigen Komplexsymbolen

$$a_{ik} = a_i\, a_k = b_i\, b_k = c_i\, c_k = \ldots,$$

wobei also $b, c, \ldots$ mit a äquivalent ist. Ebenso seien $\beta, \gamma, \ldots$ mit α; $q, r, \ldots$ mit p u. s. w. äquivalent.

Nach dem ersten Hauptsatz der symbolischen Methode ist dann jede ganze rationale projektive Invariante der Geraden (1) ein Produkt von Klammerfaktoren der Gestalt $f = (a\, \alpha\, p\, \pi\, \varrho)$, über die man eine Reihe von Voraussetzungen machen kann u. zw.:

a. Jedes f hat die Gestalt $(apma^2)$, enthält also mindestens zwei gleiche Reihen. In

$$J = (a\, \alpha\, p\, \pi\, \varrho)\, (a \ldots) \ldots$$

lässt sich nämlich die Reihe a des zweiten Faktors in den ersten hineinbringen[1]).

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[1] Vgl. meine "Invariantentheorie", Groningen, p. 79, (1923).

b. Ein Faktor $(a^2 b \ldots)$ gibt Null, da die a_{ik} die Koordinaten einer Geraden sind.

c. Dasselbe gilt für Faktoren $(abc\,..)$; denn bringt man in diesen z. B. die zweite Reihe a, so enthält das Umformungsergebnis $(a^2 c\,..)$ oder $(a^2 b\,..)$.

Bei einem Faktor der Gestalt $(pa^2 \alpha^2)$ werden wir die Koordinaten $(S'_{12})_i$ des Verbindungsraumes S'_{12} der Geraden a und α als neue Reihe einführen, sodass

$$(pa^2\,\alpha^2) = (pS'_{12}) = (pS'_{21}) \quad \ldots\ldots\ldots \quad (2)$$

wird. Wir setzen also

$$(S'_{12})_1 = +\,4\,(a_{23}\,\alpha_{45} + a_{24}\,\alpha_{53} + a_{25}\,\alpha_{34})$$
$$(S'_{12})_2 = -\,4\,(a_{13}\,\alpha_{45} + a_{14}\,\alpha_{53} + a_{15}\,\alpha_{34}) \quad \text{u. s. w.}$$

Dieser Abmachung zufolge kann jetzt auch eine Reihe a in Linearfaktoren (aS'_{ik}) auftreten. Hierdurch bleiben die obigen Bemerkungen (*a*), (*b*) und (*c*) ungeändert und es stellen sich Invarianten der Gestalt

$$A_{1,ik,rs} = (aS'_{ik})\,(aS'_{rs}) = -\,A_{1,rs,ik} \quad \ldots\ldots \quad (3)$$

ein. Hier müssen i, k, r und $s \neq 1$ und überdies $ik \neq rs$ sein. Wir haben z. B.

$$A_{1,23,45} = (aS'_{23})\,(aS'_{45}) = (a\alpha^2\,p^2)\,(am^2\,\varphi^2).$$

Bringen wir hier die Reihe a des zweiten Faktors in den ersten, so ergibt sich

$$A_{1,23,45} + A_{2,31,45} + A_{3,12,45} = 0 \quad \ldots\ldots\ldots \quad (4)$$

Eine analoge Gleichung gibt die zyklische Symmetrie bezüglich der Indizes 1, 4 und 5.

Stehen nur vier verschiedene Indizes zur Verfügung, ist also z. B. 2 mit 4 äquivalent, so fällt in Gleichung (4) der mittlere Term weg und es wird

$$A_{1,23,25} = -\,A_{3,12,25} = -\,A_{5,23,12} \quad \ldots\ldots\ldots \quad (5)$$

Die Einführung der Reihen S' gibt dann zu zwei weiteren Bemerkungen Veranlassung:

d. Ein Faktor $(ab\,.\,m^2)$ ist Reduzent. Bringt man nämlich in

$$J = (ab\,.\,m^2)\,(a \ldots.) \ldots.$$

die Reihe a aus dem zweiten Faktor in den ersten, so ergibt sich wegen (*b*) die Reihe S'_{14}.

e. Ein Faktorenpaar $(a\,..\,m^2)\,(a\,..\,n^2)$, wo n mit m äquivalent ist, ist ein Reduzent. Auch hier führt die Vereinigung der beiden Reihen a zur Reihe S'_{14}.

§ 2. *Vier Geraden.*

Die bisherigen Bemerkungen ergeben mühelos die Invarianten von vier Geraden im R_4 (Zwei und drei Geraden haben keine projektiven Invarianten im R_4).

Wir haben hier neben (3) und der in den Gleichungen (10) behandelten Möglichkeit die Ansätze:

$$J_1 = (a\alpha\, pm^2)\,(a\ldots\pi^2)$$

und

$$J_2 = (a\alpha\, pm^2)\,(aS'_{ik}).$$

Bei J_1 kann π^2 nach Bemerkung (*e*) kein n^2 sein, also z. B. $\pi^2 = \beta^2$ und

$$J_1 = (a\alpha\, pm^2)\,(axy\beta^2),$$

wobei x und y nach Bemerkung (*d*) nicht mit a äquivalent sein können. Bringt man hier die zweite Reihe a in den ersten Klammerfaktor, so tritt die Reihe S'_{14} auf, bis auf den Term

$$(a^2\alpha\, pm)\,(mxy\beta^2).$$

Hier können x und y nach Bemerkung (*b*) nicht mit β und nach Bemerkung (*d*) nicht mit m äquivalent sein. Also bleibt $x, y = p, q, r$, d.h. Reduktion nach Bemerkung (*d*).

Bei J_2 hingegen wird

$$J_2 = (a\alpha\, pm^2)\,(aS'_{ik})\,(\alpha S'_{rs})\,(pS'_{hj}).$$

Wäre hier einer der Indizes i, k, r, s, h oder j gleich 4, z. B. $i = 4$, so gäbe die Umformung von $(a\alpha pm^2)\,(aS'_{4k})$, wobei wieder die zweite Reihe a in den Klammerfaktor gebracht wird, eine neue Reihe S'_{14}, also Reduktion. Für J_2 bleibt also nur die Möglichkeit

$$J_2 = (a\alpha\, pm^2)\,(aS'_{23})\,(\alpha S'_{13})\,(pS'_{12})\, . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (6)$$

Hier bringen wir zuerst wieder die Reihe a in den Klammerfaktor, was Reduktion auf

$$J'_2 = (\alpha pma^2)\,(mS'_{23})\,(\alpha S'_{13})\,(pS'_{12})$$

gibt. Jetzt bringen wir die zweite Reihe α in den Klammerfaktor, wodurch J'_2 auf die Invarianten (5) reduziert wird. Hierdurch ist bewiesen, dass vier Geraden im R_4 keine anderen projektiven Invarianten haben als die der Gestalt (5) oder

$$A_{1,24,23} = (aS'_{24})\,(aS'_{23}) = (a\alpha^2 m^2)\,(a\beta^2 p^2) \quad . \quad . \quad . \quad . \quad . \qquad (7)$$

Es gibt im Ganzen zwölf dieser Invarianten, die sich vermöge der Umformung (5) durch vier unabhängige ausdrücken lassen, z. B. durch [1]:

$$\left.\begin{aligned} A_1 &= (mS'_{13})\,(mS'_{12}) \\ A_2 &= (aS'_{23})\,(aS'_{24}) \\ A_3 &= (\alpha S'_{13})\,(\alpha S'_{34}) \\ A_4 &= (pS'_{14})\,(pS'_{24}) \end{aligned}\right\} \quad \ldots\ldots\ldots \quad (8)$$

Die sechs Räume S'_{ik} sind voneinander linear-abhängig. Wir haben die Identität

$$\Sigma\,(S'_{13}\,S'_{14}\,S'_{34}\,S'_{42}\,S'_{23})\,(xS'_{12}) = \Sigma\,\Omega_{12}\,(xS'_{12}) = 0, \quad \ldots \quad (9)$$

wobei die Ω_{ik} die fünfreihigen Minoren der Matrix

$$\|\, S'_{12}\,S'_{13}\,S'_{14}\,S'_{34}\,S'_{42}\,S'_{23} \,\|$$

darstellen. Für diese Invarianten erhält man

$$\left.\begin{aligned} \Omega_{12} &= -4\,A_3\,A_4 & \Omega_{34} &= -4\,A_1\,A_2 \\ \Omega_{13} &= -4\,A_2\,A_4 & \Omega_{42} &= -4\,A_1\,A_3 \\ \Omega_{14} &= -4\,A_2\,A_3 & \Omega_{23} &= -4\,A_1\,A_4 \end{aligned}\right\} \quad \ldots\ldots \quad (10)$$

Man beweist dann leicht, dass die zu den vier Geraden a, α, p und m *assoziierte Gerade* dargestellt wird durch die Gleichung

$$G_5 = \frac{G_1}{A_1} + \frac{G_2}{A_2} + \frac{G_3}{A_3} + \frac{G_4}{A_4} = 0, \quad \ldots\ldots \quad (11)$$

wo z. B. G_1 durch $\Sigma\, a_{ik}\, \pi'_{ik} = 0$ gegeben ist.

§ 3. *Die Rationalbasis.*

Man kann leicht beweisen, dass bei einer beliebigen Anzahl von Geraden $a, \alpha, p, \ldots$ in allgemeiner Lage die Invarianten der Gestalt (4)

$$A_{1,23,45} = (aS'_{23})\,(aS'_{45}) = (a\alpha^2\,p^2)\,(am^2\,\varphi^2) \quad \ldots\ldots \quad (12)$$

eine *Rationalbasis* bilden.

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[1] Vgl. hierzu meine Arbeit in den Wiener Ber. 119 (1910), S. 43—54, wo ich die dualen Invarianten von vier Ebenen bestimmt habe; diese Invarianten finden sich bereits in Grassmannscher Darstellungsweise bei E. MÜLLER, Wiener Ber. 118 (1909), S. 1047—1076, allerdings ohne den Beweis ihrer Vollständigkeit.

In der genannten Arbeit von mir ist $\alpha = -A_2$, $\beta = -A_3$, $\gamma = -A_4$, $\sigma = +A_1$ und in der genannten Arbeit von E. MÜLLER ist $\mathrm{a}_1 = A$, $\mathrm{a}_2 = -A_2$, $\mathrm{a}_3 = A_3$ und $\mathrm{a}_4 = -A_4$.

Zum Beweise dieser Tatsache beschauen wir die Gerade a als Schnittgebiet der drei Räume S'_{12}, S'_{13} und S'_{14}. Ihre Gleichung wird dann

$$K = (\pi'^2 S'_{12} S'_{13} S'_{14}) = 2(\pi S'_{12})(\pi S'_{13})(\pi S'_{14}) = 2(\pi a^2 \alpha^2)(\pi b^2 p^2)(\pi c^2 m^2) = 0. \quad (13)$$

Bringen wir hier alle drei Reihen π in den ersten Klammerfaktor, so entsteht

$$K = \tfrac{1}{6}(\pi^3 a^2) \,.\, (\alpha S'_{13})(\alpha S'_{14}),$$

d. h. es gilt identisch in allen π_{ijk}

$$(\pi S'_{12})(\pi S'_{13})(\pi S'_{14}) = \tfrac{1}{6}(\pi a')^3 \,.\, (\alpha S'_{13})(\alpha S'_{14}),$$

oder, ohne die π_{ijk}:

$$a'_{ijk} \,.\, A_{2,13,14} = (S'_{12} S'_{13} S'_{14})_{ijk} \,. \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

Man kann daher in einer Komitante mit $a_{rs} = a'_{ijk}$ diese Grössen nach Multiplikation mit $A_{2,13,14}$ durch Determinanten mit drei Reihen S'_{ik} ersetzen. Bei Invarianten führt dies schliesslich auf rationale Ausdrücke in den Typen (12); denn aus Reihen S'_{ik} allein sind nur Klammerfaktoren der Gestalt (10) als Invarianten möglich. Diese letzteren zerfallen aber nach der Gleichung

$$(S'_{12} S'_{ik} S'_{hj} S'_{rs} S'_{uv}) = \Sigma\, (a^2 \alpha^2)_{i_1 \ldots i_4} (S'_{ik} S'_{hj} S'_{rs} S'_{uv})_{i_1 \ldots i_4} =$$

$$= \begin{vmatrix} (aS'_{ik}) & (aS'_{hj}) & (aS'_{rs}) & (aS'_{uv}) \\ (aS'_{ik}) & (aS'_{hj}) & (aS'_{rs}) & (aS'_{uv}) \\ (\alpha S'_{ik}) & (\alpha S'_{hj}) & (\alpha S'_{rs}) & (\alpha S'_{uv}) \\ (\alpha S'_{ik}) & (\alpha S'_{hj}) & (\alpha S'_{rs}) & (\alpha S'_{uv}) \end{vmatrix} = 4\, \Sigma\, A_{1,ik,hj} \,.\, A_{2,rs,uv}.$$

§ 4. *Fünf Geraden.*

Auch hier halten wir fest an der Einführung der Reihen S'_{ik} vermöge Gleichung (2) und beschauen eine Invariante J als reduzibel, wenn sie sich ganz-rational auf die Typen (12) zurückführen lässt. Es ergeben sich dann analog wie bei vier Geraden die Ansätze:

$$\left.\begin{aligned} J_1 &= (a\alpha p m^2)(axy\pi^2) \\ J_2 &= (a\alpha p m^2)(aS'_{ik})(\alpha S'_{rs})(pS'_{hj}) \end{aligned}\right\} \,. \quad . \quad . \quad . \quad . \quad . \quad (15)$$

Bei J_1 haben wir vorerst wieder die Möglichkeiten $\pi^2 = \beta^2$ oder $= q^2$. Sei $\pi^2 = \beta^2$, also

$$J_1 = (axy\beta^2)(a\alpha p m^2) \ldots .$$

Vereinigen wir hier die beiden Reihen a im ersten Klammerfaktor, so entsteht eine Reihe S'_{12} ausser im Terme $(a^2 xy\beta)(\beta\alpha p m^2)$; hier führt aber der zweite Klammerfaktor nach Bemerkung (d) zur Reduktion.

Somit bleibt bei J_1, da nach Bemerkung (e) $\pi^2 \neq n^2$ sein muss, nur der Ansatz $\pi^2 = \varphi^2$, also

$$J_1 = (a\alpha pm^2)(axy\,\varphi^2) = -(axy\,\varphi^2)(a\alpha pm^2) \quad \ldots \quad (16)$$

Hier gilt $x, y \neq \psi$ (Bemerkung (b)) und $x, y \neq b$ (Bemerkung (d)), also $x, y = \alpha, \beta, p$ oder q. Dies gibt die Möglichkeiten

$$\left.\begin{aligned} J_1' &= (a\alpha pm^2)(a\alpha p\varphi^2) = A_{123,45} \\ J_1'' &= (a\alpha pm^2)(a\alpha q\varphi^2) \\ J_1''' &= (a\alpha pm^2)(a\beta q\varphi^2). \end{aligned}\right\} \quad \ldots \quad (17)$$

Hier ist J_1' bereits eine Invariante, linear in allen fünf Geraden. Die beiden anderen kann man auf dieselbe Weise behandeln, was wir z. B. bei J_1'' ausführen. Wir haben

$$J_1'' = (a\alpha pm^2)(a\alpha q\varphi^2)(pu')(qv') \ldots, \quad \ldots \quad (18)$$

wobei an Stelle der Linearfaktoren (pu'), (qv') auch Klammerfaktoren $(p\,..\,\sigma^2)$, $(q\,..\,\tau^2)$ stehen können.

Wir bringen in (18) die zweite Reihe p in den ersten Klammerfaktor und die zweite Reihe q in den zweiten Klammerfaktor. Dies führt neben neuen Reihen S' auf den Term

$$(p^2 a\alpha m)(q^2 a\alpha\varphi),$$

der nach Bemerkung (e) reduzibel ist. Damit ist der Ansatz (17) erledigt.

Bei J_2 von (15) haben wir bereits eine Invariante. Wir beweisen, dass sie reduzibel ist. Zuerst kann keiner der Indizes bei den S' eine 4 sein. Denn in

$$(a\alpha pm^2)(aS'_{i4})$$

gäbe z. B. die Zusammenziehung der Reihen a im Klammerfaktor eine neue Reihe S'_{14}. Somit bleiben die Möglichkeiten $i, k = 2, 3, 5$, dann $r, s = 1, 3, 5$ und $h, j = 1, 2, 5$. Wäre z. B. $ik = 25$, so würden wir in J_2 vorerst die Reihen α im Klammerfaktor vereinigen, was auf

$$(\alpha^2 a pm)(aS'_{25})(mS'_{rs})(pS'_{hj})$$

führt. Bringen wir hier die zweite Reihe a in den Klammerfaktor, so entsteht Reduktion.

Bei fünf Geraden gibt es also ausser den Invarianten der Gestalt (12) nur noch den Typus J_1' von (17):

$$A_{123,45} = (a\alpha pm^2)(a\alpha p\varphi^2) \quad \ldots \quad (18)$$

Wir werden im folgenden § zeigen, dass auch er reduzibel ist.

§ 5. *Die unabhängigen Invarianten A.*

Was zunächst die Invarianten (12) oder

$$A_{1,23,45} = (aS'_{23})(aS'_{45}) = (a\alpha^2 p^2)(am^2 \varphi^2)$$

betrifft, haben wir Symmetrie in 23, in 45 und schiefe Symmetrie in den Paaren 23, 45. Ferners nach (4) zyklische Symmetrie in den Indizes 123 und ebenso bezüglich 145.

Mit Hilfe dieser zyklischen Symmetrie kann man zunächst jede Invariante $A_{i,jk,rs}$ mit $i = 4, 5$ auf solche mit $i = 1, 2, 3$ zurückführen. Von den 15 möglichen Invarianten $A_{i,jk,rs}$ bleiben dann die folgenden neun übrig:

$$\left.\begin{array}{lll} J_1 = A_{1,23,45} & J_4 = A_{2,13,45} & J_7 = A_{3,13,45} \\ J_2 = A_{1,24,35} & J_5 = A_{2,14,35} & J_8 = A_{3,14,25} \\ J_3 = A_{1,25,34} & J_6 = A_{2,15,34} & J_9 = A_{3,15,24} \end{array}\right\} \quad . \quad . \quad (19)$$

Aus allen zyklischen Symmetrien ergeben sich dann noch drei unabhängige Gleichungen

$$\left.\begin{array}{r} J_1 + J_4 + J_7 = 0 \\ J_1 + J_5 + J_6 + J_8 + J_9 = 0 \\ J_1 + J_2 + J_3 + J_4 + J_5 + J_6 = 0 \end{array}\right\}, \quad . \quad . \quad . \quad . \quad (20)$$

sodass man also von den 9 Invarianten (19) noch drei weglassen kann und sechs linear-unabhängige behält, z.B. J_1, J_2, J_3, J_4, J_5 und J_8. Dass diese tatsächlich linear-unabhängig sind beweist man durch den Ansatz mit konstanten λ_i

$$\lambda_1 J_1 + \lambda_2 J_2 + \ldots + \lambda_8 J_8 = 0;$$

lässt man hier je zwei der fünf Geraden zusammenfallen, so ergeben sich für die λ_i lineare Gleichungen, aus denen $\lambda_i = 0$ folgt.

Bei den Invarianten $A_{123,45}$ von (18) haben wir Symmetrie in 123 und schiefe Symmetrie in 45. Bringen wir ferner die beiden Reihen a in den ersten Klammerfaktor, so entsteht

$$A_{123,45} = -A_{423,15} + \tfrac{1}{2} A_{3,14,25} + \tfrac{1}{2} A_{2,14,35} \quad . \quad . \quad . \quad . \quad (21)$$

Hieraus entnehmen wir, dass jede Invariante $A_{ijk,rs}$ auf $A_{123,45}$ und die $A_{i,jk,rs}$ reduzierbar ist. Dass aber $A_{123,45}$ selbst auf die $A_{i,jk,rs}$ reduziert werden kann, lässt sich wie folgt zeigen. Bringen wir in

$$A = (m^2\, a\alpha p)(\varphi^2\, a\alpha p)$$

durch zweimalige Umformung die beiden Reihen φ in den ersten Klammerfaktor, so entsteht wegen

$$(\varphi^2 a a p)(m^2 a a p) = -(m^2 a a p)(\varphi^2 a a p) = -A$$

die Gleichung

$$4A = A_{1,24,35} + A_{1,34,25} + A_{2,14,35} + A_{2,34,15} + A_{3,14,25} + A_{3,24,15}\,, \quad . \quad (22)$$

oder, mit der Bezeichnung (19):

$$4A_{123,45} = J_2 - J_3 + J_5 - J_6 + J_8 - J_9 . \quad . \quad . \quad . \quad . \quad (22a)$$

Wir haben also auch bei fünf Geraden im R_4 *keine anderen Invarianten als die vom Typus* $A_{i,jk,rs}$.

Physics. — *The isotopic constitution of nickel and chromium.* By Miss W. A. LUB. (Communicated by Prof. P. ZEEMAN).

(Communicated at the meeting of February 25, 1939.)

Nickel.

In order to try to clear up the discrepancy of the results of the experiments about the isotopic constitution of nickel, which has remained between the mass analysis of ASTON [1]), the parabola analysis by DE GIER and ZEEMAN [2]) and the results of the experiments of DEMPSTER [3]), we have reexamined the experiments about nickel with the mass spectrograph of our laboratory.

ASTON found an excellent agreement of the parabola analysis of Ni by DE GIER and ZEEMAN with his own experiments, except for Ni 61.

DEMPSTER observed with nickel of exceptional purity made by fractionating nickel carbonyl, as supplied by Hilger, the masses at 58, 60, 61, 62 and 64, as isotopes of nickel and indicated the lines at 61 and 64 being of approximately equal intensity in all the photographs.

After these publications we have examined once more the photographs taken by ZEEMAN and DE GIER, but neither the photographs, nor the photograms we took from some plates indicated a trace of mass 61, though the dispersion of our mass spectrograph was sufficient to detect an isotope of mass 61 with equal abundance of isotope 64.

Our first photographs showed just the same aspects as those taken by DE GIER and ZEEMAN: though the parabola of mass 64 was always present, no trace of 61 could be found. After augmenting the intensity of the bundle, without broadening the canal, we got on our plate an indication of a parabola between those of masses 60 and 62.

As the intensity of this new parabola seems to be very small, it was rather difficult to obtain good photographs for measurements. With narrow slits the intensities obtained during a suitable time of exposure were too small to get other parabolas than those already known, while by experimenting with wide slits, the possibility that 61 will be overshadowed by 60 is rather great.

By choosing the opening of the canal suitable for this problem, we could make our lines sharper, and then we obtained eight photographs on which the new parabola was clearly visible. Among these eight photographs there were five which could be used for measurements; all these giving 61 for the mass.

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[1]) F. W. ASTON, Proc. Roy. Soc. A., **149**, 401 (1935); Nature, **137**, 613 (1936).

[2]) J. DE GIER and P. ZEEMAN, Proc. Kon. Akad. v. Wetensch., Amsterdam, **38**, 810 (1935).

[3]) A. J. DEMPSTER, Phys. Rev., **50**, 98 (1936).

The reproduction of one of these plates shows clearly the isotope 61 [1]).

These photographs were partly taken with the same sample of nickel carbonyl as used by ZEEMAN and DE GIER partly by another. Both samples were highly pure, so that we could not detect impurities on our plates. By diluting the nickel carbonyl with a suitable dose of oxygen, we can obtain photographs practically free of carbon hydrides. We value the intensity of 61 with regard to 64 as ± 1 : 10.

The revised figure for percentage abundance looks as follows:

Mass number	58	60	61	62	64
% abundance	68.0	27.2	0.1	3.8	0.9

Using the new value of the packing fraction of Ni as indicated by ASTON [2]), and the change of scale as given by SMYTHE [3]), we obtain for the atomic weight 58.69; the international value being 58.69.

In addition to the parabolas of nickel we always get the groups of parabolas for Ni C, Ni CO, $Ni(CO)_2$, $Ni(CO)_3$ and $Ni(CO)_4$. On two photographs we also find a parabola for the mass 89, which could be explained as $^{61}Ni\ ^{12}C\ ^{16}O$. Nevertheless we must take into account another explanation of the parabola of mass 89: the molecule $^{60}Ni\ ^{13}C\ ^{16}O$ has practically the same mass. The relative abundance of $^{13}C : ^{12}C = 1 : 99$, being of the same order of magnitude as those of $^{61}Ni : ^{60}Ni$. We must expect the parabola 89 being partly due to the molecule $^{60}Ni\ ^{13}C\ ^{16}O$. This will explain the fact that the intensity of 89 with respect to 88 is greater than those of 61 with respect to 60.

Chromium.

Among the isotopes predicted by MATTAUCH [4]) we see an isotope of chromium ^{56}Cr. SITTE [5]) in his scheme of isotopes indicated ^{56}Cr as already known. Probably this will be due to a misprint, for in literature we could not find an indication about this isotope and also the table of HAHN [6]) about "the chemical elements and their natural isotopes" for 1938, showed for Cr only the four isotopes as given by ASTON [7]).

Mass number	50	52	53	54
% abundance	4.9	81.6	10.4	3.1

Thank to the valuable gift of Prof. Dr. W. HIEBER, München, who sent

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[1]) It must be remarked, that the ratio of blackening of the different parabolas has suffered by reproduction.

[2]) F. W. ASTON, Nature, **141**, 1096 (1938).

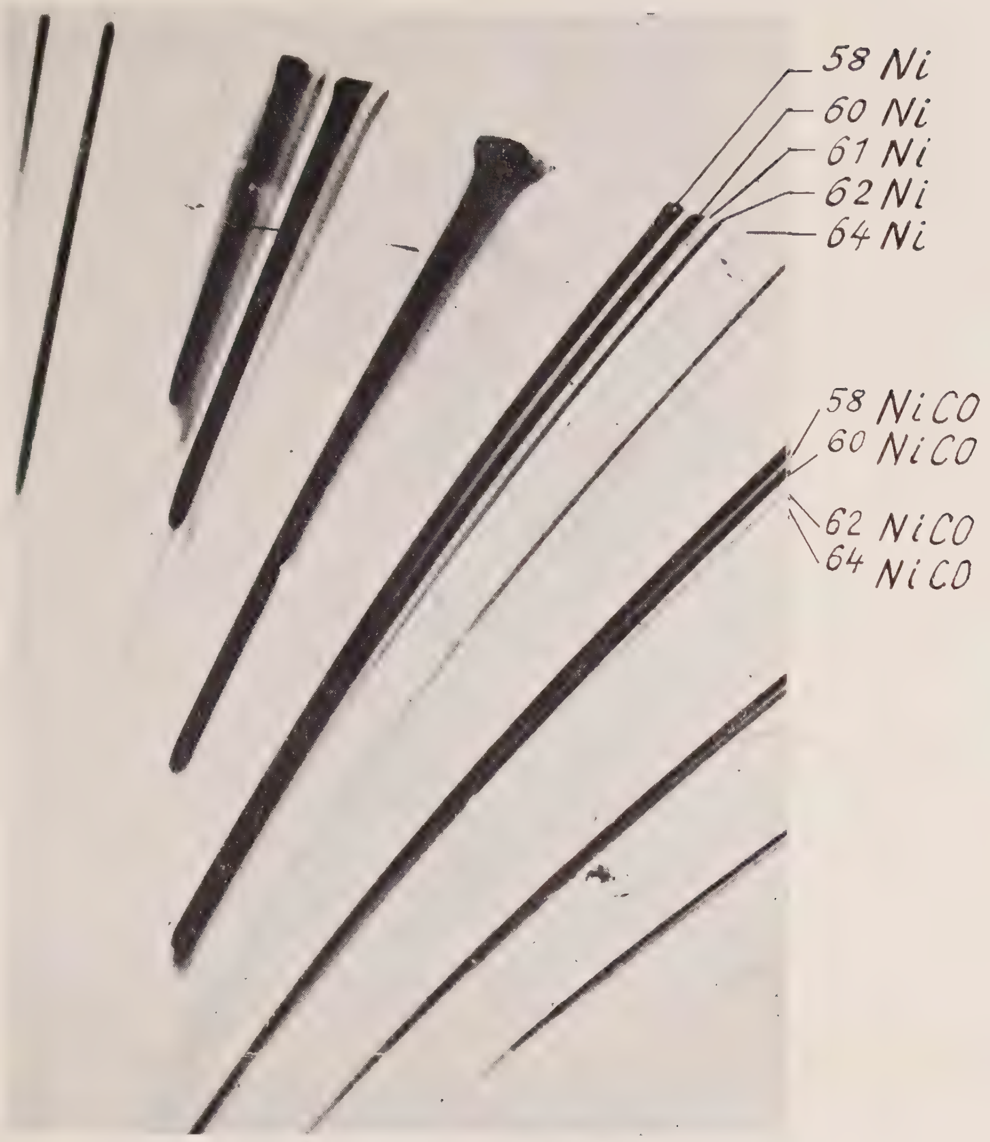
[3]) W. R. SMYTHE, Phys. Rev., **45**, 299 (1934).

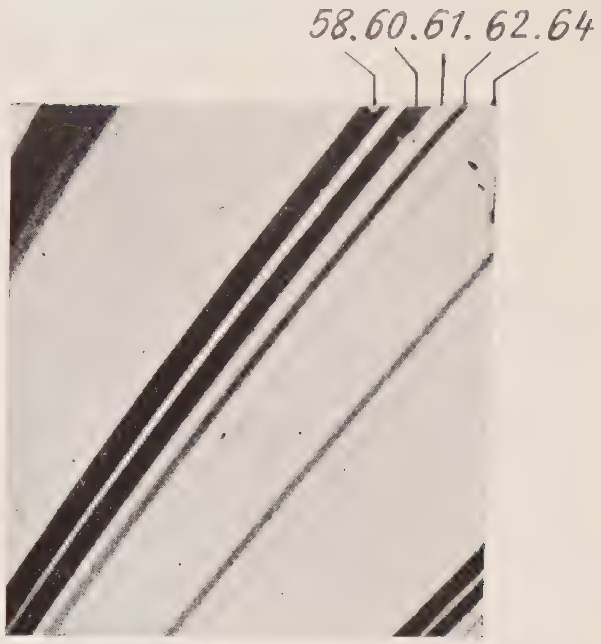
[4]) J. MATTAUCH, Zs. f. Phys., **91**, 361 (1934).

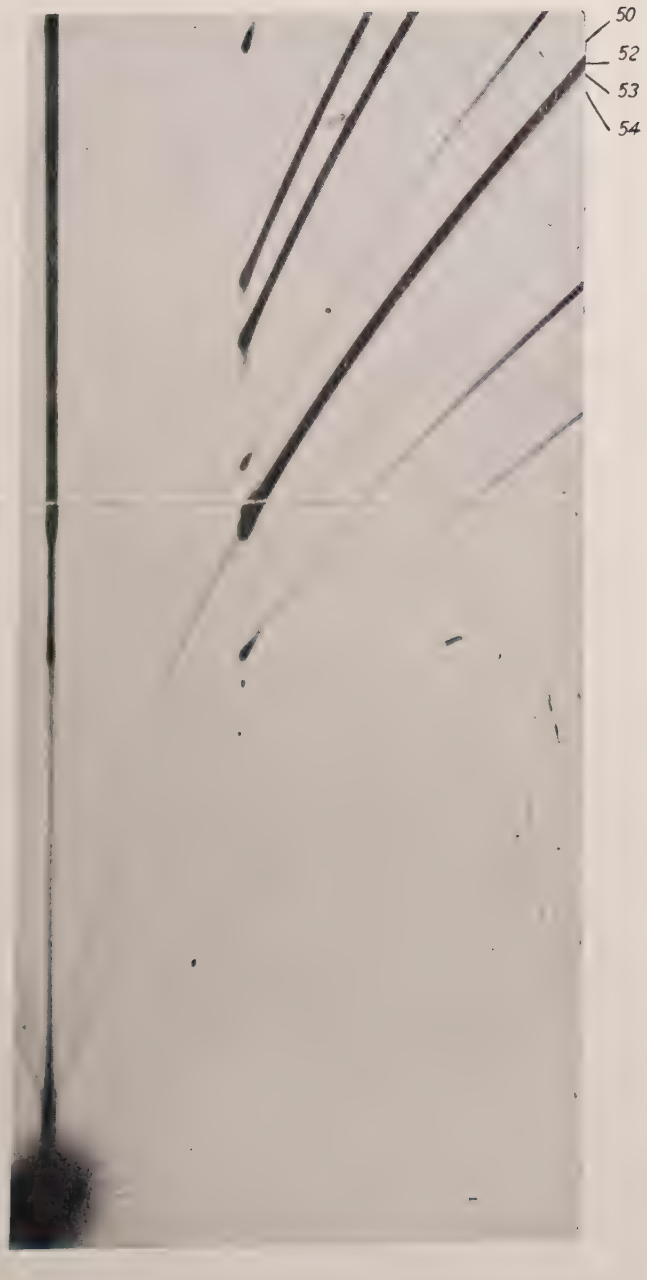
[5]) K. SITTE, Zs. f. Phys., **96**, 512 (1935).

[6]) O. HAHN, Ber. D. Chem. Ges., **71**, 1 (1938).

[7]) F. W. ASTON, Nature, **126**, 200 (1930); Proc. Roy. Soc. London A **130**, 302 (1931).


58 Ni
60 Ni
61 Ni
62 Ni
64 Ni
58 NiCO
60 NiCO
62 NiCO
64 NiCO


58.60.61.62.64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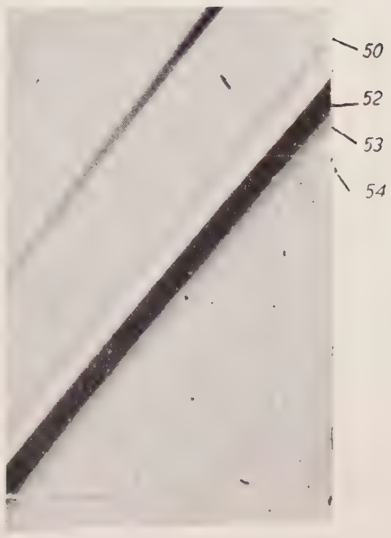
50
52
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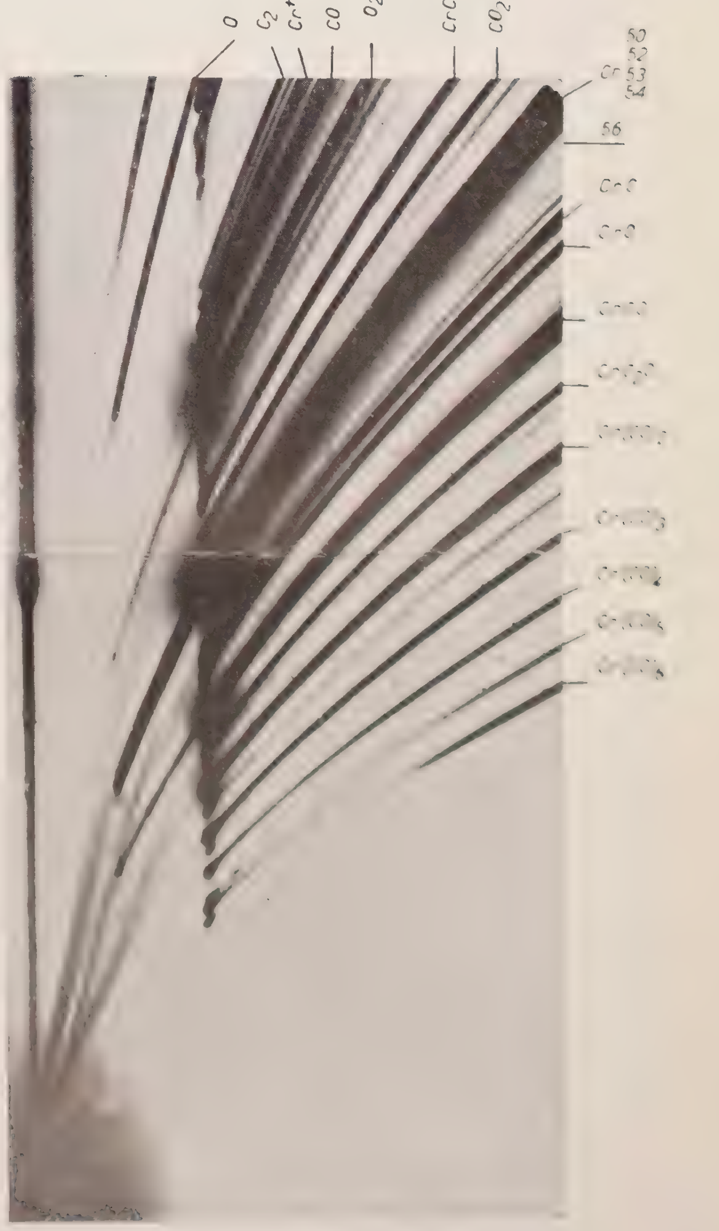
0
C2
Cr++
CO
O2
CrCO++
CO2
50
52
Cr 53
54
56
CrC
CrO
CrCO

us some tens milligrams $Cr(CO)_6$, we could study the isotopic constitution of chromium by means of this volatile compound. The vapour pressure of the solid carbonyl is much lower than those of the nickel carbonyl, but it is sufficient for use in the discharge tube. By diluting with oxygen, method used with success by DE GIER and ZEEMAN by their experiments with other carbonyls, we could get a rather constant discharge.

Our first attempts did not seem to be very successfull, an exposure of one hour being needed to obtain a photograph of the four isotopes already known.

By replacing the head of the cathode by another one of more suitable form, and by adjusting the tube of discharge in such a way that the intensity of the bundle canalrays reaches a maximum, we could reduce the time of exposure for the isotopes 50, 52, 53 and 54, to one minute. Now an exposure of half an hour gave a slight trace of an isotope of mass 56. As the difference in intensity between the four isotopes and these of mass 56 seems to be rather great, it was somewhat difficult to obtain plates suited for measurements. By experimenting with extreme low pressure in camera and slitscanal, we could obtain four photographs which showed the parabola of mass 56. By varying the time of exposure, we could evaluate the intensity of this parabola to $^1/_{100}$ of the intensity of the parabola 50. This indicates the percentage abundance of this mass to 0.5 $^0/_{00}$.

But if ^{56}Cr exists, it is isobar with ^{56}Fe, the strongest isotope of iron. We therefore must be sure that this parabola is not originated by an impurity in the chromium carbonyl. A micro analysis of this carbonyl, which Mr. F. DE BOER was so kind to perform for us by means of a three step colorimeter of Leitz, showed an abundance of 0.2 $^0/_{00}$ Fe in this sample.

As the quantity of the carbonyl at our disposal was rather limited, we could not make more experiments about this question.

In this phase of the experiments we can only conclude: Though the parabola 56 will partly be due to ^{56}Fe, the existence of the isotope ^{56}Cr with a percentage abundance of 0.3 $^0/_{00}$ seems still probable.

In conclusion it is a great pleasure to me to thank Prof. Dr. P. ZEEMAN for his great interest and encouragement through the course of the work, Prof. Dr. W. HIEBER who provided the specimen of the chromium carbonyl, Mr. F. DE BOER for his microchemical analysis of the carbonyl, and Mr. J. v. D. ZWAAL for the great care bestowed on the reproduction of the photographs.

Summary.

The isotopic constitution of nickel and chromium was studied.

Nickel: In agreement with the results of the experiments of ASTON and DEMPSTER, we could prove the existence of ^{61}Ni. But this isotope is found

with a much smaller abundance than indicated by DEMPSTER. We found the ratio of the intensities of ^{61}Ni : ^{64}Ni, as 1 : 10.

For nickel is found:

Mass number	58	60	61	62	64
% abundance	68.0	27.2	0.1	3.8	0.9

For Chromium:

The existence of the new isotope of chromium ^{56}Cr is indicated as very probable.

Laboratory "Physica" of the University of Amsterdam.

February 1939.

Mathematics. — *Ueber eine Differentialinvariante zweiter Ordnung der binären kubischen Differentialform.* Von P. G. MOLENAAR.

(Communicated by Prof. R. WEITZENBÖCK).

(Communicated at the meeting of February 25, 1939.)

Die binäre kubische Differentialform $f = a^3_{dx}$ besitzt vier relative lineare Differentialkovarianten l, L_1, L_2 und L_3. [1]).

Mit Hilfe der Diskriminante R kann man hieraus absolute Kovarianten formen. Die Rotation dieser Kovarianten erzeugt dann *Differentialinvarianten zweiter Ordnung.*

Auf diese Weise wird hier aus l eine Invariante J^* abgeleitet. $J^* = 0$ ist die notwendige und hinreichende Bedingung dafür, dass a^3_{dx} in die Form $K(x_1\, x_2) \,.\, \{dx_1^3 + dx_2^3\}$ transformiert werden kann.

Die Differentialkovariante

$$l_{dx} = (\varphi\,\psi)\,(\varphi\, a)^2\,(a\,\alpha)\,\alpha_{dx} - (\varphi\,\alpha)^2\,(\varphi\, a)\,(\psi\, a)\, a_{dx} \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$

oder

$$l_{dx} = \left(-a_{122}\,\alpha_{22}\,\frac{\partial a_{111}}{\partial x_1} + \dots\right) dx_1 + \left(-a_{222}\,\alpha_{22}\,\frac{\partial a_{111}}{\partial x_1} + \dots\right) dx_2$$

ist vom Gewichte 6.

Die Diskriminante $R = (\alpha\,\beta)^2$ ist ebenfalls vom Gewichte 6.

Der Quotient

$$l^*_{dx} = \frac{l_{dx}}{R} \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (2)$$

ist also eine *absolute* Differentialkovariante. Ihre Rotation

$$J^* = \frac{\partial l_1^*}{\partial x_2} - \frac{\partial l_2^*}{\partial x_1} = \frac{1}{R}\left(\frac{\partial l_1}{\partial x_2} - \frac{\partial l_2}{\partial x_1}\right) - \frac{1}{R^2}\left(l_1\,\frac{\partial R}{\partial x_2} - l_2\,\frac{\partial R}{\partial x_1}\right) . \; . \quad (3)$$

ist daher eine *Differentialinvariante zweiter Ordnung.*

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[1]) Vgl. P. G. MOLENAAR, Proc. Kon. Ned. Akad. v. Wetensch., Amsterdam, **42**, 158—166 (1939).

Wegen der wiederholten Differentiation ist es zweckmässig die folgenden Symbole zu gebrauchen:

$$\frac{\partial a_{ikl}}{\partial x_m} = \dot{a}_i\,\dot{a}_k\,\dot{a}_l\,\lambda_m = \dot{b}_i\,\dot{b}_k\,\dot{b}_l\,\mu_m = \ldots = \dot{a}_{ikl}\,\lambda_m = \dot{b}_{ikl}\,\mu_m = \ldots$$

$$\frac{\partial \alpha_{ik}}{\partial x_m} = \dot{\alpha}_i\,\dot{\alpha}_k\,\sigma_m = \dot{\beta}_i\,\dot{\beta}_k\,\tau_m = \dot{\gamma}_i\,\dot{\gamma}_k\,\nu_m = \ldots = \dot{\alpha}_{ik}\,\sigma_m = \dot{\beta}_{ik}\,\tau_m = \dot{\gamma}_{ik}\,\nu_m = \ldots$$

$$\frac{\partial Q_{ikl}}{\partial x_m} = \dot{Q}_i\,\dot{Q}_k\,\dot{Q}_l\,\varrho_m = \dot{Q}_{ikl}\,\varrho_m = \ldots$$

$$\frac{\partial^2 a_{ikl}}{\partial x_m\,\partial x_n} = \ddot{a}_i\,\ddot{a}_k\,\ddot{a}_l\,\lambda_m\,\lambda_n = \ddot{a}_{ikl}\,\lambda_m\,\lambda_n = \ldots \qquad \text{u. s. w.}$$

Mit dieser Bezeichnung wird z. B.:

$$\alpha_{ik} = (a\,b)^2\,a_i\,b_k \qquad Q_{ikl} = (b\,\alpha)\,b_{ik}\,\alpha_l \qquad (Q\,a)^3 = (b\,\alpha)\,(b\,a)^2\,(\alpha\,a)$$

$$\dot{\alpha}_{ik}\,\sigma_m = (\dot{a}\,b)^2\,\dot{a}_i\,b_k\,\lambda_m + (a\,\dot{b})^2\,a_i\,\dot{b}_k\,\mu_m = (\dot{a}\,b)^2\,(\dot{a}_i\,b_k + \dot{a}_k\,b_i)\,\lambda_m$$

$$\dot{Q}_{ikl}\,\varrho_m = (\dot{b}\,\alpha)\,\dot{b}_{ik}\,\alpha_l\,\mu_m + (b\,\dot{\alpha})\,b_{ik}\,\dot{\alpha}_l\,\sigma_m,$$

also

$$\begin{aligned}(\dot{Q}\,\dot{a})^3\,(\varrho\,\lambda) &= (\dot{b}\,\alpha)\,(\dot{b}\,\dot{a})^2\,(\alpha\,\dot{a})\,(\mu\,\lambda) + (b\,\dot{\alpha})\,(b\,\dot{a})^2\,(\dot{\alpha}\,\dot{a})\,(\sigma\,\lambda) = \\ &= (\dot{a}\,\alpha)\,(\dot{a}\,\dot{b})^2\,(\alpha\,\dot{b})\,(\lambda\,\mu) - (\dot{a}\,b)^2\,(\dot{a}\,\dot{\alpha})\,(b\,\dot{\alpha})\,(\sigma\,\lambda) = \\ &= 0 - \tfrac{1}{2}\,(\dot{\beta}\,\dot{\alpha})\,(\dot{\beta}\,\dot{\alpha})\,(\sigma\,\tau) = 0 \quad \ldots\ldots\ldots \quad (4)\end{aligned}$$

oder nicht-symbolisch:

$$\left(\frac{\partial Q_0}{\partial x_1}\frac{\partial a_3}{\partial x_2} - \frac{\partial Q_0}{\partial x_2}\frac{\partial a_3}{\partial x_1}\right) - 3\left(\frac{\partial Q_1}{\partial x_1}\frac{\partial a_2}{\partial x_2} - \frac{\partial Q_1}{\partial x_2}\frac{\partial a_2}{\partial x_1}\right) +$$
$$+ 3\left(\frac{\partial Q_2}{\partial x_1}\frac{\partial a_1}{\partial x_2} - \frac{\partial Q_2}{\partial x_2}\frac{\partial a_1}{\partial x_1}\right) - \left(\frac{\partial Q_3}{\partial x_1}\frac{\partial a_0}{\partial x_2} - \frac{\partial Q_3}{\partial x_2}\frac{\partial a_0}{\partial x_1}\right) = 0.$$

Mit Hilfe dieser Symbole findet man für (1)

$$l_{dx} = (\dot{a}\,\lambda)\,(\dot{a}\,b)^2\,(b\,\alpha)\,\alpha_{dx} - (\dot{a}\,\alpha)^2\,(\dot{a}\,b)\,(\lambda\,b)\,b_{dx}.$$

Nun ist weiter:

$$\begin{aligned}&(\dot{a}\,\lambda)\,(\dot{a}\,b)^2\,(b\,\alpha)\,\alpha_{dx} = \\ &\quad = \tfrac{1}{2}\,(\dot{a}\,b)^2\,(\dot{a}\,\lambda)\,(b\,\alpha)\,\alpha_{dx} + \tfrac{1}{2}\,(\dot{a}\,b)^2\,(b\,\lambda)\,(\dot{a}\,\alpha)\,\alpha_{dx} - \tfrac{1}{2}\,(\dot{a}\,b)^2\,(b\,\dot{a})\,(\lambda\,\alpha)\,\alpha_{dx} = \\ &\quad = \tfrac{1}{2}\,(\dot{a}\,b)^2\,\{(\dot{a}\,\lambda)\,(b\,\alpha) + (b\,\lambda)\,(\dot{a}\,\alpha)\}\,\alpha_{dx} + \tfrac{1}{2}\,(\dot{a}\,b)^3\,(\lambda\,\alpha)\,\alpha_{dx} = \\ &\quad = \tfrac{1}{2}\,(\dot{\beta}\,\tau)\,(\dot{\beta}\,\alpha)\,\alpha_{dx} + \tfrac{1}{2}\,(\dot{a}\,b)^3\,(\lambda\,\alpha)\,\alpha_{dx} = \tfrac{1}{2}\,(\dot{\alpha}\,\sigma)\,(\dot{\alpha}\,\beta)\,\beta_{dx} + \tfrac{1}{2}\,(\dot{a}\,b)^3\,(\lambda\,\alpha)\,\alpha_{dx}.\end{aligned}$$

Da $(a\alpha)^2 a_i \equiv 0$ $(i = 1, 2)$, ist ferner

$$\begin{aligned}(\dot{a}\alpha)^2 (\dot{a}b)(\lambda b)\, b_{dx} &= -(a\dot{\alpha})^2 (ab)(\sigma b)\, b_{dx} = \\ &= -(a\dot{\alpha})(\sigma\dot{\alpha})(ab)^2 b_{dx} + (a\dot{\alpha})(\sigma a)(ab)(\dot{\alpha}b)\, b_{dx} = \\ &= -(\beta\dot{\alpha})(\sigma\dot{\alpha})\,\beta_{dx} - \tfrac{1}{2}(ab)(\dot{\alpha}a)(\dot{\alpha}b)\,\{(\sigma a)\, b_{dx} - (\sigma b)\, a_{dx}\} = \\ &= -(\dot{\alpha}\sigma)(\dot{\alpha}\beta)\,\beta_{dx} + \tfrac{1}{2}(\dot{\alpha}\beta)^2 \sigma_{dx},\end{aligned}$$

also

$$l_{dx} = \tfrac{3}{2}(\dot{\alpha}\beta)(\dot{\alpha}\sigma)\,\beta_{dx} - \tfrac{1}{2}(\dot{\alpha}\beta)^2 \sigma_{dx} + \tfrac{1}{2}(\dot{a}b)^3 (\lambda\alpha)\,\alpha_{dx} \quad . \quad . \quad . \quad (5)$$

Dem letzten Glied von (5) kann man eine andere Gestalt geben, denn wir haben

$$\begin{aligned}(\dot{a}b)^3 (\lambda\alpha)\,\alpha_{dx} &= (\dot{a}b)^2 (\lambda b)(\dot{a}\alpha)\,\alpha_{dx} - (\dot{a}b)^2 (\lambda\dot{a})(b\alpha)\,\alpha_{dx} = \\ &= (\dot{Q}b)^2 (\varrho b)\,\dot{Q}_{dx} - (ab)^2 (\sigma b)(a\dot{\alpha})\,\dot{\alpha}_{dx} - (\dot{a}Q)^2 (\lambda\dot{a})\, Q_{dx} = \\ &= (a\dot{Q})^2 (\varrho a)\,\dot{Q}_{dx} - (\dot{a}Q)^2 (\lambda\dot{a})\, Q_{dx} - (\sigma\beta)(\beta\dot{\alpha})\,\dot{\alpha}_{dx} = \\ &= (\dot{a}Q)^2 (\dot{a}\lambda)\, Q_{dx} - (a\dot{Q})^2 (a\varrho)\,\dot{Q}_{dx} + (\dot{\alpha}\beta)^2 \sigma_{dx} - (\dot{\alpha}\beta)(\dot{\alpha}\sigma)\,\beta_{dx},\end{aligned}$$

also

$$l_{dx} = (\dot{\alpha}\beta)(\dot{\alpha}\sigma)\,\beta_{dx} + \tfrac{1}{2}(\dot{a}Q)^2 (\dot{a}\lambda)\, Q_{dx} - \tfrac{1}{2}(a\dot{Q})^2 (a\varrho)\,\dot{Q}_{dx} \quad . \quad . \quad (6)$$

Man findet nun leicht

$$\begin{aligned}\frac{\partial l_1}{\partial x_2} - \frac{\partial l_2}{\partial x_1} &= (\ddot{\alpha}\beta)(\ddot{\alpha}\sigma)(\beta\sigma) + (\dot{\alpha}\dot{\beta})(\dot{\alpha}\sigma)(\dot{\beta}\tau) + \tfrac{1}{2}(\ddot{a}Q)^2 (\ddot{a}\lambda)(Q\lambda) + \\ &\quad + \tfrac{1}{2}(\dot{a}\dot{Q})^2 (\dot{a}\lambda)(\dot{Q}\varrho) - \tfrac{1}{2}(\dot{a}\dot{Q})^2 (\dot{a}\varrho)(\dot{Q}\lambda) - \tfrac{1}{2}(a\ddot{Q})^2 (a\varrho)(\ddot{Q}\varrho) = \\ &= (\ddot{\alpha}\beta)(\ddot{\alpha}\sigma)(\beta\sigma) + \tfrac{1}{2}(\ddot{a}Q)^2 (\ddot{a}\lambda)(Q\lambda) - \tfrac{1}{2}(a\ddot{Q})^2 (a\varrho)(\ddot{Q}\varrho) + \\ &\qquad\qquad + \tfrac{1}{2}(\dot{a}\dot{Q})^2 \{(\dot{a}\lambda)(\dot{Q}\varrho) - (\dot{a}\varrho)(\dot{Q}\lambda)\} = \\ &= (\ddot{\alpha}\beta)(\ddot{\alpha}\sigma)(\beta\sigma) + \tfrac{1}{2}(\ddot{a}Q)^2 (\ddot{a}\lambda)(Q\lambda) - \tfrac{1}{2}(a\ddot{Q})^2 (a\varrho)(\ddot{Q}\varrho) + \\ &\qquad\qquad + \tfrac{1}{2}(\dot{a}\dot{Q})^3 (\lambda\varrho),\end{aligned}$$

also wegen (4)

$$\frac{\partial l_1}{\partial x_2} - \frac{\partial l_2}{\partial x_1} = (\ddot{\alpha}\beta)(\ddot{\alpha}\sigma)(\beta\sigma) + \tfrac{1}{2}(\ddot{a}Q)^2 (\ddot{a}\lambda)(Q\lambda) - \tfrac{1}{2}(a\ddot{Q})^2 (a\varrho)(\ddot{Q}\varrho). \quad (7)$$

Aus $R = (\alpha\beta)^2 = (\gamma\vartheta)^2$ folgt $\dfrac{\partial R}{\partial x_i} = 2(\dot{\alpha}\beta)^2 \sigma_i = 2(\dot{\gamma}\vartheta)^2 \nu_i$ also nach (6)

$$\begin{aligned}l_1 \frac{\partial R}{\partial x_2} - l_2 \frac{\partial R}{\partial x_1} &= 2(\dot{\alpha}\beta)(\dot{\alpha}\sigma)(\beta\nu)(\dot{\gamma}\vartheta)^2 + \\ &\quad + (\dot{a}Q)^2 (\dot{a}\lambda)(Q\sigma)(\dot{\alpha}\beta)^2 - (a\dot{Q})^2 (a\varrho)(\dot{Q}\sigma)(\dot{\alpha}\beta)^2 \quad . \quad . \quad . \quad . \quad (8)\end{aligned}$$

somit ergibt sich die Differentialinvariante (3)

$$J^* = \frac{1}{R}\left\{(\ddot{\alpha}\,\beta)(\ddot{\alpha}\,\sigma)(\beta\,\sigma) + \tfrac{1}{2}(\ddot{a}\,Q)^2(\ddot{a}\,\lambda)(Q\,\lambda) - \tfrac{1}{2}(a\,\ddot{Q})^2(a\,\varrho)(\ddot{Q}\,\varrho)\right\} -$$

$$- \frac{1}{R^2}\left\{2(\dot{\alpha}\beta)(\dot{\alpha}\sigma)(\beta\nu)(\dot{\gamma}\vartheta)^2 + (\dot{a}\,Q)^2(\dot{a}\lambda)(Q\,\sigma)(\dot{\alpha}\beta)^2 - (a\,\dot{Q})^2(a\varrho)(\dot{Q}\,\sigma)(\dot{\alpha}\beta)^2\right\}. \quad (9)$$

Es sei bemerkt, dass $l_1 \frac{\partial R}{\partial x_2} - l_2 \frac{\partial R}{\partial x_1}$ keinen Faktor R enthält, denn der Koeffizient von $\left(\frac{\partial a_0}{\partial x_1}\right)^2$ ist $4 a_3 \alpha_{22}(3 a_1 a_2 a_3 - 2 a_2^3 - a_0 a_3^2)$ und dieser ist nicht teilbar durch R.

$J = R^2 J^*$ ist daher eine ganze rationale Differentialinvariante.

Bringt man $f = a_{dx}^3$ auf die Normalform

$$f_n = a_0\, dx_1^3 + a_3\, dx_2^3$$

($R \neq 0$ wird vorausgesetzt, da sonst l verschwindet), so findet man aus (7) und (8)

$$\frac{\partial l_1}{\partial x_2} - \frac{\partial l_2}{\partial x_1} = a_0 a_3^2 \frac{\partial^2 a_0}{\partial x_1\,\partial x_2} - a_0^2 a_3 \frac{\partial^2 a_3}{\partial x_1\,\partial x_2} + a_3^2 \frac{\partial a_0}{\partial x_1}\frac{\partial a_0}{\partial x_2} - a_0^2 \frac{\partial a_3}{\partial x_1}\frac{\partial a_3}{\partial x_2}$$

$$l_1 \frac{\partial R}{\partial x_2} - l_2 \frac{\partial R}{\partial x_1} = 4\, a_0^2 a_3^2 \left(a_0^2 \frac{\partial a_3}{\partial x_1}\frac{\partial a_3}{\partial x_2} - a_3^2 \frac{\partial a_0}{\partial x_1}\frac{\partial a_0}{\partial x_2}\right)$$

und somit

$$J^* = \frac{1}{-2 a_0^2 a_3^2}\left(a_0 a_3^2 \frac{\partial^2 a_0}{\partial x_1\,\partial x_2} - a_0^2 a_3 \frac{\partial^2 a_3}{\partial x_1\,\partial x_2} + a_0^2 \frac{\partial a_3}{\partial x_1}\frac{\partial a_3}{\partial x_2} - a_3^2 \frac{\partial a_0}{\partial x_1}\frac{\partial a_0}{\partial x_2}\right) \quad (10)$$

Dies kann auch unmittelbar gefolgert werden aus der Normalform von l^*

$$l_n^* = \frac{l}{R} = \frac{1}{2}\left(\frac{1}{a_3}\frac{\partial a_3}{\partial x_1}\, dx_1 + \frac{1}{a_0}\frac{\partial a_0}{\partial x_2}\, dx_2\right) \quad . \quad . \quad . \quad . \quad (11)$$

$J^* = 0$ bedeutet für diese Normalform (11)

$$\frac{\partial}{\partial x_2}\left(\frac{1}{a_3}\frac{\partial a_3}{\partial x_1}\right) - \frac{\partial}{\partial x_1}\left(\frac{1}{a_0}\frac{\partial a_0}{\partial x_2}\right) = 0,$$

woraus folgt

$$\frac{a_3}{a_0} = F(x_1)\, G(x_2)$$

worin F und G Funktionen von x_1 bzw. x_2 sind. Dann ist aber

$$f_n = a_0\, dx_1{}^3 + F(x_1)\, G(x_2)\, a_0\, dx_2{}^3 = H(x_1\, x_2) \{ A(x_1)\, dx_1{}^3 + B(x_2)\, dx_2{}^3 \}.$$

Hieraus folgt, dass es eine Transformation gibt, welche f überführt in

$$\bar{f}_n = K(\bar{x}_1\, \bar{x}_2) \{ d\bar{x}_1{}^3 + d\bar{x}_2{}^3 \} \quad . \; . \; . \; . \; . \; . \; . \quad (12)$$

Ist umgekehrt a^3_{dx} von der Beschaffenheit, dass sie in die Gestalt (12) transformiert werden kann, so ist

$$l^*_n = \frac{1}{2} \left(\frac{1}{K} \frac{\partial K}{\partial x_1}\, dx_1 + \frac{1}{K} \frac{\partial K}{\partial x_2}\, dx_2 \right)$$

und daher

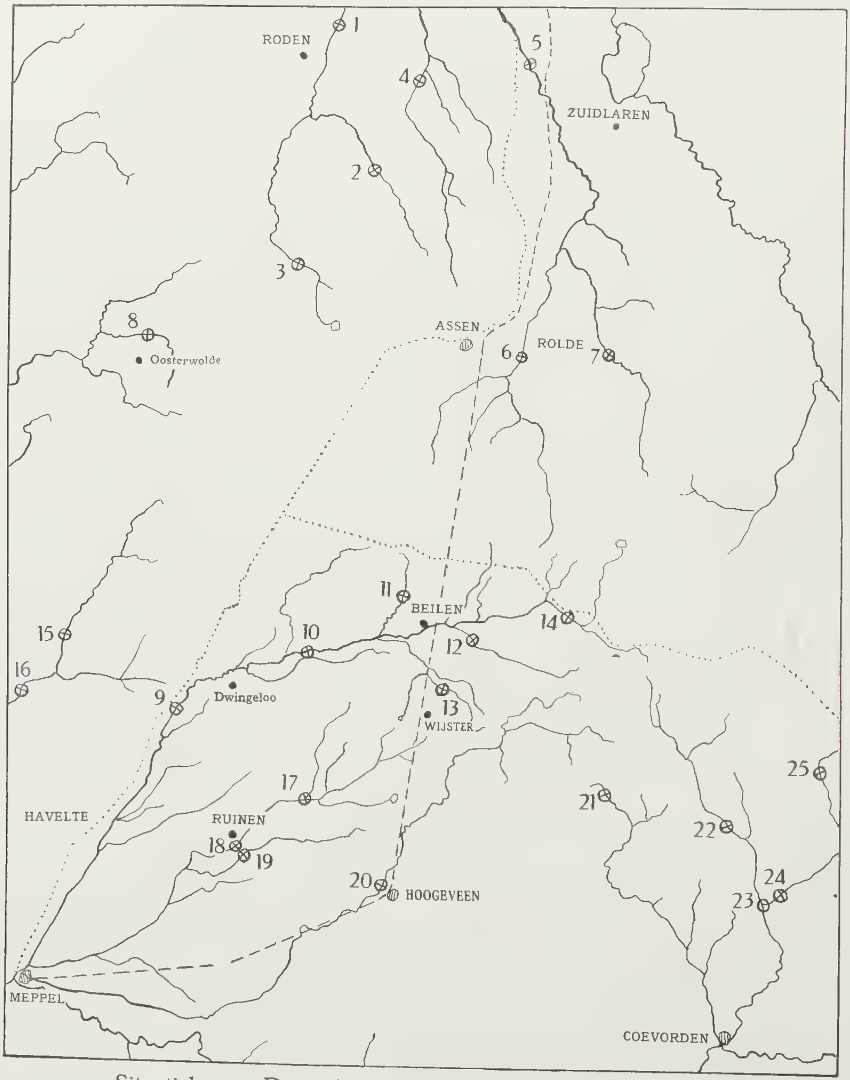
$$J^* = Rot\, l^*_n = 0.$$

$J^* = 0$ ist also die notwendige und hinreichende Bedingung dafür, dass die binäre kubische Grundform in die Gestalt (12) transformiert werden kann.

Plantkunde. — *De diatomeeënflora van de Drentsche beken.* Door W. BEIJERINCK. (Communicated by Prof. A. H. BLAAUW.)

(Communicated at the meeting of February 25, 1939.)

Tusschen de jaren 1923 en 1939 werd af en toe diatomeeënmateriaal uit Drentsche wateren, zooals heide- en veenplassen, kanalen en beken, verzameld en, na de gebruikelijke kiezelschaalreiniging met $HNO_3 + KClO_3$ en centrifugeering, in den vorm van een collectie duurzame styraxpreparaten bewaard. Uit deze verzameling is voor dit overzicht het beekmateriaal uitgekozen. De nummers op het kaartje correspondeeren met die op de



Situatiekaart. De onderzochte localiteiten zijn genummerd.

tabel. Voor een omschrijving der localiteiten zij verwezen naar den index hieronder. Men kan 3 afwatergebieden onderscheiden, n.l.: I, het naar de Waddenzee afvloeiende gebied; II, het naar het IJsselmeer en III, het naar de Ov. Vecht loozende gebied. Met de letters A, B—I zijn de afzonderlijke stroomgebieden der beken aangeduid.

Reeds in 1934 was door Mej. N. KRIJTHE een begin gemaakt met de determinatie der soorten (n.l. de no's: 4, 5, 8, 9, 10, 11, 12, 13, 15, 16, 17, 18 en 19). Thans heb ik zelf het geheele materiaal, afkomstig van 25 localiteiten, meermalen doorzocht, zoowel met olieïmmersie als met kleinere vergrootingen. De determinatie geschiedde in hoofdzaak met HUSTEDT's werken: „Bacillariophyta", in: PASCHER's Süsswasserflora (1930) en „Die Kieselalgen", in: RABENHORST's Kryptogamenflora. Onder de afgebeelde vormen zijn er enkele, die niet met zekerheid waren thuis te brengen (zie figurenverklaring). De onderzochte preparaten blijven voorloopig ter ev. revisie of contrôle bewaard op het biologisch station te Wijster (Dr.). Dat het materiaal, wat den tijd van inzameling betreft, nogal heterogeen is en sommige preparaten reeds vele jaren oud zijn, doet, gezien de uitkomsten, die wijzen op een groote constantheid in de samenstelling van het hoofdcontingent, minder ter zake. Ook voor ev. later in te stellen hernieuwde onderzoekingen kunnen deze oudere gegevens hun waarde hebben, vooral nu Drente door de ontginningen op groote schaal van karakter gaat veranderen.

Wat betreft de resultaten van dit onderzoek kan in de eerste plaats worden opgemerkt, dat er een groote groep van soorten is, die zoo geregeld en meestal ook zoo talrijk weerkeert, dat men kan spreken van een kenmerkend bestanddeel dezer beekvegetatie, al blijven natuurlijk volstrekt niet al deze soorten en vormen tot dit milieu beperkt. Ten deele zijn het meer ubiquistische en cosmopolitische vormen. Veeleer heeft men in deze eutrophe waterloopen, met hun door anthropogene invloeden reeds zoo sterk gewijzigd karakter, te doen met een samenstel van elementen der heide- en hoogveenplassen (bijv. *Tabellaria flocculosa, Frustulia rhomboides,* v. *saxonica, Eunotia lunaris* en *tenella*), der moerasvenen (bijv. *Caloneis-, Neidium-, Navicula-, Pinnularia-, Cymbella-* en *Gomphonema*-soorten), van de stilstaande wateren (zooals: *Melosira varians* en *italica, Rhopalodia-, Epithemia-, Cocconeis-, Synedra-, Surirella-* en kleine *Nitzschia*-soorten) en van de zwak stroomende wateren (bijv. *Gomphonema, Meridon, Achnanthes* en *Fragilaria*). Dit gemengde karakter komt juist tot uitdrukking bij de meest gewone soorten van dit gebied. Gedurende den zomer zijn vele beken zoover opgedroogd, dat tijdelijk stilstaand water aanwezig is of zelfs algeheele opdroging plaats heeft. Dit is een belangrijk verschil met onze grootere rivieren en stroompjes. Een tweede verschilpunt is niet zoozeer in den trophiegraad dan wel in het gehalte aan humusstoffen (dystrophie) gelegen. Ook ligt de bedding dezer beken voor een groot deel in oude moerasveenafzettingen met veel limoniet, vivianiet enz. Het gehalte aan

Tabellarisch overzicht van de in Drentsche beken aangetroffen diatomeeën. (I, II en III zijn resp. de afwatergebieden naar de Waddenzee, het IJsselmeer en de Ov. Vecht. A = Roderdiep gebied; B = Eelderdiep; C = Drentsche Aa gebied; D = Tjonger; E = Beilerstroom gebied; F = Vledder Aa; G = Ruiner Aa gebied; H = Echtener Stroompje; I = Gebied van Loo- en Drostendiep.)

Vindplaats: / Naam:	I							II														III				
	A			B	C			D	E						F		G			H	I				
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25
Melosira varians C. A. Ag.	+	+	+	+	+	+	+	.	+	.	.	.	.	.	+	+	.	.	+	+	+	+	+	+	+
Melosira italica (Ehr.) Kütz.	+	.	.	+	.	+	+	.	.	.	+	+	+	.	+	+	.	+	+	.	+	+	+	+	+
Melosira italica, v. tenuissima (Grun.) O. Müll.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	+	.	.	.	.	.	.	+	+	.
Melosira arenaria Moore	.	.	.	.	.	.	.	.	+	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.
Cyclotella Menighiniana Kütz.	+	+	+	+	+	+	+	+	+	.	.	+	.	.	+	+	+	+	.	+	.	+	+	+	+
Coscinodiscus lacustris Grun.	+	.	.	.	+	+	.	.	.	.	.	.	.	.	+	+	.	.	.	.	.	.	+	+	.
Tabellaria fenestrata (Lyngb.) Kütz.	+	+	.	+	+	+	+	+	+	.	.	.	.	+	+	+	+	+	+	+	+	+	+	+	.
Tabellaria flocculosa (Roth.) Kütz.	+	+	+	+	+	.	+	+	+	.	+	.	.	+	+	+	+	+	+	+	+	+	.	+	+
Diatoma vulgare Bory.	.	.	.	.	+	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.
Meridion circulare, v. constricta (Ralfs) v. Heurck	+	+	+	+	.	+	+	+	+	.	+	+	.	+	.	+	+	+	.	+	.	+	.	.	+
Fragilaria capucina Desm.	+	+	+	+	+	+	.	+	+	+	.	+	.	+	+	+	+	+	.	.	.	+	+	+	+
Fragilaria Harrissonii W. Smith	.	.	.	+	+	+	+	.	.	.	.	.	.	.	.	+	.	.	.	.	.	.	.	+	.
Fragilaria construens (Ehr.) Grun.	+	+	+	+	.	.	+	+	.	.	+	.	.	+	+	+	.	.	.	+	.	+	+	+	+
Fragilaria pinnata Ehr.	+	+	.	+	.	+	+	.	+	.	.	.	.	.	.	+	.	+	+	+	.	.	.	.	.
Asterionella gracillima (Hantzsch) Heiberg	.	.	.	.	+	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.
Synedra ulna (Nitzsch) Ehr.	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Synedra ulna v. impressa Hust.	.	.	.	.	.	.	.	.	.	.	.	+	.	.	.	.	.	.	.	.	.	.	.	.	.
Synedra ulna v. biceps (Kütz.)	.	+	+	.	.	.	.	+	.	.	.	+	+	.	.	+	.	.	.	.	.	+	+	+	+
Synedra ulna v. amphirhynchus (Ehr.) Grun.	.	.	.	.	.	.	.	.	.	.	+	.	.	.	.	.	.	.	.	.	.	.	.	.	.
Synedra ulna v. danica (Kütz.) Grun.	.	.	+	.	.	.	.	.	.	+	.	.	+	.	.	.	.	.	.	+	.	.	.	.	.
Synedra capitata Ehr.	.	.	.	.	.	.	.	.	+	+	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.
Synedra acus Kütz.	.	.	.	.	.	.	.	+	.	.	.	.	+	.	.	+	.	.	.	.	.	+	+	+	+
Synedra rumpens, v. familiaris (Kütz.) Grun.	.	.	.	+	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	+	.	.	+	.	+
Synedra parasitica (W. Smith)	.	.	.	.	+	.	.	.	.	.	+	.	.	.	.	.	.	.	.	.	.	.	.	.	.

Tabellarisch overzicht. *(Vervolg.)*

Vindplaats: / Naam:	I							II													III				
	A			B	C			D	E						F		G			H	I				
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25
Eunotia arcus, Ehr., kl. vorm	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	+	.	+	.	.	.	.
Eunotia tenella (Grun.) Hust.	.	.	.	.	.	.	+	.	.	.	.	+	.	+	.	.	.	.	.	.	.	.	.	.	.
Eunotia pectinalis (Kütz.) Rab.	+	+	.	.	+	.	+	.	+	+	+	.	+	.	+	+	.	+	.	+	.	+	+	+	+
Eunotia pectinalis v. minor (Kütz.) Rab.	+	+	+	.	.	.	.	+	.	.	.	+	.	+	+	+	+	+	+	.	+	.	+	.	.
Eunotia pectinalis v. undulata (Ralfs) Rab.	+	+	+	+	.	.	.	+	+	.	.	.	.	.	+	.	.	+	.	.	.	.	.	+	.
Eunotia lunaris (Ehr.) Grun.	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	.	+	+	+	+	+	+	+
Eunotia lunaris v. capitata Grun.	.	.	.	.	.	.	.	.	.	.	.	.	+	.	.	.	+	.	.	.	.	.	.	.	.
Eunotia lunaris v. subarcuata (Naeg) Grun.	+	+	+	.	.	+	+	+	.	.	.	.	.	+	.	+	+	.	+	+	+	.	.	+	.
Eunotia veneris (Kütz.) O. Müll.	.	+	.	.	.	.	.	+	+	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.
Eunotia monodon Ehr.	+	.	.	.	.	.	.	.	+	.	.	.	.	.	.	+	.	.	+	.	.	.	.	.	.
Eunotia monodon v. maior, f. bidens (W. Smith)	.	.	.	.	.	+	+	+	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.
Cocconeis pediculus Ehr.	.	.	.	+	+	+	+	+	+	.	.	.	+	.	.	+	.	.	.	.	.	.	.	+	+
Cocconeis placentula (Ehr.)	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	.	+	+	+	+	+	+
Cocconeis plac. v. euglypta (Ehr.) Cleve	+	.	.	.	.	+	.	+	.	.	.	.	.	.	.	+	.	.	.	+	.	+	+	+	+
Cocconeis plac. v. lineata (Ehr.) Cleve	.	.	.	.	+	+	.	.	.	.	.	.	.	.	.	.	.	+	.	.	.	.	.	.	.
Achnanthes exigua Grun.	.	.	.	.	.	+	+	.	.	.	.	.	.	.	.	.	+	.	.	.	.	.	.	.	.
Achnanthes lanceolata v. rostrata Hust.	+	.	+	+	+	+	+	+	+	.	.	+	+	+	.	+	+	+	+	.	+	.	+	.	+
Achnanthes lanceolata v. elliptica Cleve	+	.	.	.	+	+	+	+	.	+	.	.	+	+	.	.	+	+	+	.	.	.	+	.	.
Mastogloia Brauni Grun.	.	.	.	.	.	.	.	.	.	.	.	+	.	.	.	.	.	.	.	.	.	.	.	.	.
Frustulia rhomboides v. saxonica (de Toni) Rab.	+	.	.	.	.	.	.	+	.	.	.	.	.	.	.	.	+	+	.	.	+	+	.	.	.
Frustulia vulgaris Twaites	+	+	+	+	.	+	.	+	.	.	.	.	.	+	+	.	+	+	.	+	.	.	+	.	.
Gyrosigma acuminatum (Kütz.) Rab.	.	.	.	.	+	.	.	.	.	+	+	.	.	.	+	+	.	.	.	.	.	+	+	.	.
Caloneis amphisbaena (Bory) Cleve	.	+	.	+	.	+	+	+	.	.	+	+	.	.	+	+	.	+	+	+	+	.	+	+	.
Caloneis silicula (Ehr.) Cleve	.	+		+	+	+	+	+	.	.	+	+	.	.	+	+	+	+	.	+	.	+	+	.	+
Caloneis bacillum (Grun.) Mereschkovsky	.	.	.	.	.	.	+	+	.	.	.	.	.	.	+	.	.	.	.	.	.	.	.	.	.

Tabellarisch overzicht. *(Vervolg.)*

Vindplaats:	I							II													III				
	A			B	C			D	E						F		G			H	I				
Naam:	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25
Neidium affine v. amphirhynchus (Ehr.) Cleve	.	+	.	.	.	+	+	+	+	.	.	.	.	.	+	+	.	+	+	.	.	.	.	.	.
Neidium iridis (Ehr.) Cleve	+	.	.	+	.	+	+	.	.	.	+	.	.	.	.	+	.	.	+	.	+	.	.	.	.
Neidium iridis, f. vernalis Reichelt	.	.	.	+	.	.	.	+	.	.	.	+	.	.	.	+	.	+	+	.	.	.	.	.	.
Neidium productum (W. Smith) Cleve	+	+	+	+	+	+	+	+	+	.	+	+	.	.	+	+	+	+	+	+	.	+	+	+	+
Neidium dubium (Ehr.) Cleve	.	.	.	.	.	+	.	+	.	.	+	+	.	.	.	+	.	+	+	.	+	.	.	.	.
Neidium dubium, ovale vorm	.	.	.	.	.	.	.	.	.	.	.	.	.	.	+	.	.	.	.	.	.	.	.	.	.
Neidium dubium, constricta Hust.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	+	.	.	.	.	.	.	.	.	.	.
Diploneis ovalis (Hilse) Cleve	.	+	.	.	.	.	+	.	.	.	.	+	.	.	.	.	.	.	.	.	.	.	.	.	.
Diploneis interrupta (Kütz.) Cleve, kl. vorm	.	.	+	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.
Stauroneis phoenicenteron Ehr.	+	+	+	+	+	+	+	+	+	.	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Stauroneis anceps Ehr.	+	+	+	+	.	+	+	+	+	.	+	+	.	+	+	.	+	+	+	+	+	+	+	+	+
Stauroneis Smithii Grun.	+	+	+	+	+	.	+	+	+	.	+	+	+	+	+	+	+	+	.	+	.	.	.	.	.
Stauroneis Smithii, v. incisa Pant.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	+	.	.	.	.	.
Stauroneis legumen Ehr.	+	.	.	.	+	.	+	.	.	.	.	.	.	.	.	.	.	.	+	.	.	.	.	.	.
Stauroneis parvula Grun.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	+		.	.	.	.	.
Navicula cuspidata, v. ambigua (Ehr.) Cleve	+	+	.	+	.	+	+	+	+	.	+	+	.	.	+	+	.	+	+		.	+	.	.	+
Navicula cuspidata Kütz.	.	.	.	.	.	.	.	.	.	.	.	+	.	.	.	.	.	.	.	.	.	.	.	.	.
Navicula pupula, v. rectangularis (Greg.)	+	+	+	+	+	+	+	+	+	.	+	+	.	+	+	+	+	+	+	+	.	+	+	+	+
Navicula pupula, v. elliptica Hust Grun.	+	.	+	+	+	.	.	.	.	.	.	+	.	.	+	+	+	+	.	+	.	.	.	+	.
Navicula rhynchocephala Kütz.	+	+	+	+	+	+	+	+	+	+	+	+	.	+	+	+	+	+	+	+	.	+	+	+	+
Navicula viridula, v. slesviscensis (Grun.) Cleve	+	+	+	+	+	+	+	+	+	.	+	.	.	+	+	+	+	+	+	+	+	+	.	+	+
Navicula radiosa Kütz.	+	.	+	+	+	+	+	+	+	+	+	+	.	+	.	+	+	+	+	+	.	+	+	+	+
Navicula menisculus Schumann	+	+	+	+	+	+	+	+	+	.	.	.	.	+	+	+	+	+	+	+	+	+	+	+	+
Navicula dicephala (Ehr.) W. Smith	+	+	+	+	.	+	+	+	.	.	+	+	.	+	+	+	+	+	+	+	+	+	+	+	+
Navicula dicephala v. neglecta (Krasske) Hust.	.	.	.	.	.	.	+	.	.	.	.	.	.	.		+	.	.	.	.	.	.	.	.	.
Navicula gastrum Ehr.	+	.	.	+	.	+	+	+	.	.	+	+	.	+	+	+	+	+	+	.	.	+	+	+	+
Navicula oblonga Kütz.	.	.	.	.	+	.	+	.	.	.	+	.	.	.	.	.	.	.	.	.	.	+	+	.	.

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Navicula integra (W. Smith) Ralfs	.	.	.	.	+	.	+	.	.	.	.	.	.	.	+	.	+	+	+	.	+	.	.	.	.
Navicula hungarica, v. capitata (Ehr.) Cleve	+	.	+	+	+	+	+	.	.	.	+	.	.	.	.	.	.	+	+	.	.	.	+	.	+
Navicula cryptocephala Kütz.	.	.	.	.	.	+	+	.	.	.	.	+	.	+	+	.	.	.	+	.	.	.	.	.	.
Navicula minima Grun.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	+	.	.	.	.	.	.	.	.	.	.
Pinnularia subcapitata Greg.	+	+	.	.	.	.	.	.	.	.	.	.	.	.	+	+	.	.	.	+	.	.	.	.	.
Pinnularia subcap. v. Hilseana (Jan) O. Müll.	.	.	+	.	+	.	.	+	.	.	.	.	.	.	+	+	.	+	+	+		.	.	.	.
Pinnularia mesolepta (Ehr.) W. Smith	+	.	+	.	+	.	.	.	.	.	+	+	.	.	+	+	+	+	.	.		.	.	.	.
Pinnularia microstauron (Ehr.) Cleve	.	+	.	.	.	.	.	.	.	.	.	.	.	.	.	.	+	.	.	.		.	+	+	.
Pinnularia f. biundulata O. Müll.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	+	+	.	.		.	.	.	.
Pinnularia borealis Ehr.	+	.	+	+	+	.	.	+	+	.	.	+	.	.	.	.	.	+	+	.	.	.	.	.	.
Pinnularia lata (Bréb.) W. Smith	.	+	+	.	.	+	+	.	.	.	.	.	.	.	.	.	.	.	.	.	+	.	.	.	.
Pinnularia interrupta W. Smith	.	.	.	+	.	.	+	.	.	.	.	.	.	.	.	.	.	.	.	.	+	+	.	+	.
Pinnularia gibba Ehr.	+	+	+	+	.	.	.	+	.	.	.	.	.	+	+	+	.	.	+	.	+	+	.	.	.
Pinnularia gibba f. subundulata Mayer	+	+	+	.	+	.	+	.	.	.	.	+	.	.	+	+	+	+	+	.	.	.	.	.	+
Pinnularia major (Kütz.) Cleve	+	+	.	+	.	+	+	.	.	.	.	+	.	.	+	+	+	+	+	.	+	+	+	+	+
Pinnularia viridis (Nitzsch) Ehr.	+	+	+	+	+	+	+	+	+	+	.	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Pinnularia nobilis Ehr.	.	+	.	+	.	+	.	.	.	.	.	+	.	.	+	.	+	+	+	.	.	.	.	.	+
Pinnularia cardinalis (Ehr.) W. Smith	.	.	+	.	.	+	.	.	.	.	.	+	.	.	+	.	+	.	.	.	.	.	.	.	.
Pinnularia legumen Ehr.	.	.	.	.	.	+	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.
Amphora ovalis Kütz. (incl. vormen)	+	+	.	+	+	+	+	+	+	.	+	+	+	+	+	+	+	+	+	+	.	+	+	+	+
Cymbella naviculiformis Auerswald	+	+	+	+	+	+	+	+	+	.	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Cymbella cuspidata Kütz.	+	+	+	+	+	+	+	.	+	.	.	.	+	.	+	+	+	+	+	+	.	+	+	+	+
Cymbella turgida (Greg.) Cleve ?	.	.	.	.	.	.	.	+	.	+	+	.	.	.	.	.	.	.	.	.	.	.	.	.	.
Cymbella ventricosa Kütz. ?	.	.	.	.	+	.	.	.	.	.	.	+	.	.	.	.	.	.	.	.	.	.	.	.	.
Cymbella affinis Kütz.	+	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.
Cymbella cistula (Hempr.) Grun.	.	.	.	.	.	.	.	.	+	+	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.
Cymbella lanceolata (Ehr.) v. Heurck	.	.	.	.	.	.	.	.	.	+	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.

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Cymbella aspera (Ehr.) Cleve	+	+	+	.	+	+	+	+	+	+	+	+	.	+	+	+	+	+	+	+	.	+	+	+	+
Cymbella cymbiformis (Kütz.) v. Heurck ?	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	+	.	.	.	.	.	.	.	.	.
Gomphonema acuminatum Ehr.	+	+	.	+	.	+	.	+	+	+	+	+	+	+	+	+	+	+	+	.	.	+	+	+	+
Gomphonema acum. v. Brébissonii (Kütz.) Cleve	.	.	.	.	+	.	.	.	.	.	.	.	.	.	+	.	+	.	+	.	.	.	.	.	.
Gomphonema acum. v. trigonocephala (Ehr.) Grun.	.	+	.	+	.	.	.	+	.	.	.	+	.	+	+	+	+	+	.	.	+	.	+	+	+
Gomphonema acum. v. turris (Ehr.) Cleve	.	.	.	.	.	.	.		.	.	.	+	.	.	.	.	.	.	+	.	.	.	.	.	.
Gomphonema augur Ehr.	.	.	.	.	.	.	.	.	.	+	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.
Gomphonema angustatum v. producta Grun.	+	+	.	+	.	+	+	+	+	.	.	+	+	+	+	+	+	+	+	.	+	+	+	+	.
Gomphonema gracile Ehr.	+	+	.	.	.	.	.	.	.	+	+	.	+	+	.	.	.	.	.	.	.	.	.	.	.
Gomphonema constrictum Ehr.	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	.	+	+	+	+
Gomphonema bohemicum Reichelt–Fricke	+	+	.	.	+	+	+	+	.	+	+	+	+	+	+	+	+	+	+		.	+	+	+	+
Gomphonema olivaceum v. calcarea Cleve	.	.	+	.	.	.	.	.	.	+	+	+	.	.	.	.	.	.	.	.	.	.	.	.	.
Gomphonema longiceps Ehr.	.	.	.	.	.	.	.	+	.	.	.	.	.	.	.	+	.	.	.	+	.	.	.	.	.
Epithemia zebra (Ehr.) Kütz.	.	.	.	+	.	.	.	+	+	.	.	+	+	.	+	+	.	+	.	.	.	+	+	+	+
Epithemia zebra v. saxonica (Kütz.) Grun.	.	.	.	+	.	.	.	.	.	+	+	.	.	.	.	.	.	.	.	+	.	.	.	.	+
Epithemia zebra v. porcellus (Kütz.) Grun.	.	.	.	.	+	.	.	.	.	+	.	.	+	.	.	.	.	+	.	+	.	.	.	.	.
Epithemia turgida (Ehr.) Kütz.	+	+	.	+	.	+	+	+	.	+	+	+	.	+	+	+	.	+	.	.	.	.	.	.	+
Epithemia turgida, v. granulata (Ehr.) Grun.	.	.	.	.	.	.	.	.	.	+	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.
Rhopalodia gibba (Ehr.) O. Müll.	.	.	.	+	.	.	.	+	.	+	.	+	+	.	+	+	.	+	.	.	.	.	+	+	+
Rhopalodia gibba, v. ventricosa (Ehr.) Grun.	.	.	.	.	.	.	.	.	.	+	.	+	+	.	+	+	+	.	.	.	.	.	+	+	+
Hantzschia amphioxys (Ehr.) Grun.	.	+	.	+	+	+	+	+	+	.	.	.	.	.	.	.	+	+	.	+	.	+	+	.	.
Nitzschia stagnorum Rab. ?	.	.	.	.	.	.	.	+	.	.	+	.	.	.	.	.	.	.	.	.	.	.	.	.	.
Nitzschia recta Hantzsch. ?	.	+	.	.	.	.	.	+	.	.	.	.	.	.	.	.	+	.	.	.	.	.	.	.	.
Nitzschia palea (Kütz.) W. Smith	.	.	.	.	+	.	+	.	.	.	+	+	.	.	+	+	+	.	.	+	.	.	+	+	+
Nitzschia linearis W. Smith	.	.	.	.	.	.	+	+	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.
Nitzschia tryblionella, v. victoriae Grun.	.	.	.	+	+	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	+	.	.

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Nitzschia subtilis (Kütz.) Grun.	+	+	+	.	.	+	+	+	+	.	+	.	.	.	.	+	+	+	+	+	+	+	+	+	+
Nitzschia sigmoidea (Ehr.) W. Smith	+	+	.	+	.	.	.	+	+	.	+	+	.	.	+	+	.	+	+	+	.	+	+	.	+
Nitzschia scalaris (Ehr.) W. Smith	+	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.
Nitzschia ignorata Krasske	.	.	.	.	+	.	+	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	+
Cymatopleura solea (Bréb.) W. Smith	+	+	.	+	+	+	+	+	+	.	+	+	+	+	+	+	+	+	+	+	.	+	+	+	+
Cymatopleura solea, v. regula (Ehr.) Grun.	.	.	.	.	.	.	.	+	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.
Cymatopleura elliptica (Bréb.) W. Smith	.	+	.	+	+	+	.	.	+	+	+	.	.	.	+	+	.	+	.	+	.	+	+	+	.
Cymatopleura elliptica v. hibernica (W. Smith) Hust.	+	.	.	.	.	+	.	.	.	.	.	.	.	.	.	+	.	+	.	.	.	.	.	.	.
Surirella biseriata Bréb.	.	.	.	.	.	+	.	+		.	.	.	.	.	.	+	.	.	.	.	.	+	+	+	.
Surirella biseriata, v. bifrons (Ehr.) Hust.	.	.	.	.	.	.	.	.	+	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.	.
Surirella linearis W. Smith	+	+	+	+	+	.	.	+	+	.	+	+	+	+	+	+	+	+	+	+	+	.	+	+	+
Surirella linearis v. constricta (Ehr.) Grun.	.	.	.	.	.	.	.	.	.	+	.	.	.	.	.	.	.	.	.	.	.	.	.	+	+
Surirella robusta Ehr.	+	+	.	+	+	+	.	+	.	.	+	.	.	+	+	+	+	.	+	+	.	+	+	+	+
Surirella elegans Ehr.	.	.	.	.	.	.	+	.	.	.	.	.	.	.	.	.	.	+	.	.	.	.	.	.	.
Surirella ovata Kütz.	+	+	.	+	.	.	.	.	+	.	+	.	.	.	+	.	.	+	.	.	.	.	.	.	.

colloïdale Fe-, Al- en Si-verbindingen is dan ook vaak belangrijk. Ten slotte komen hierbij de meststoffen van het cultuurland.

Onder de meer zeldzame soorten komen nog twee merkwaardige groepen

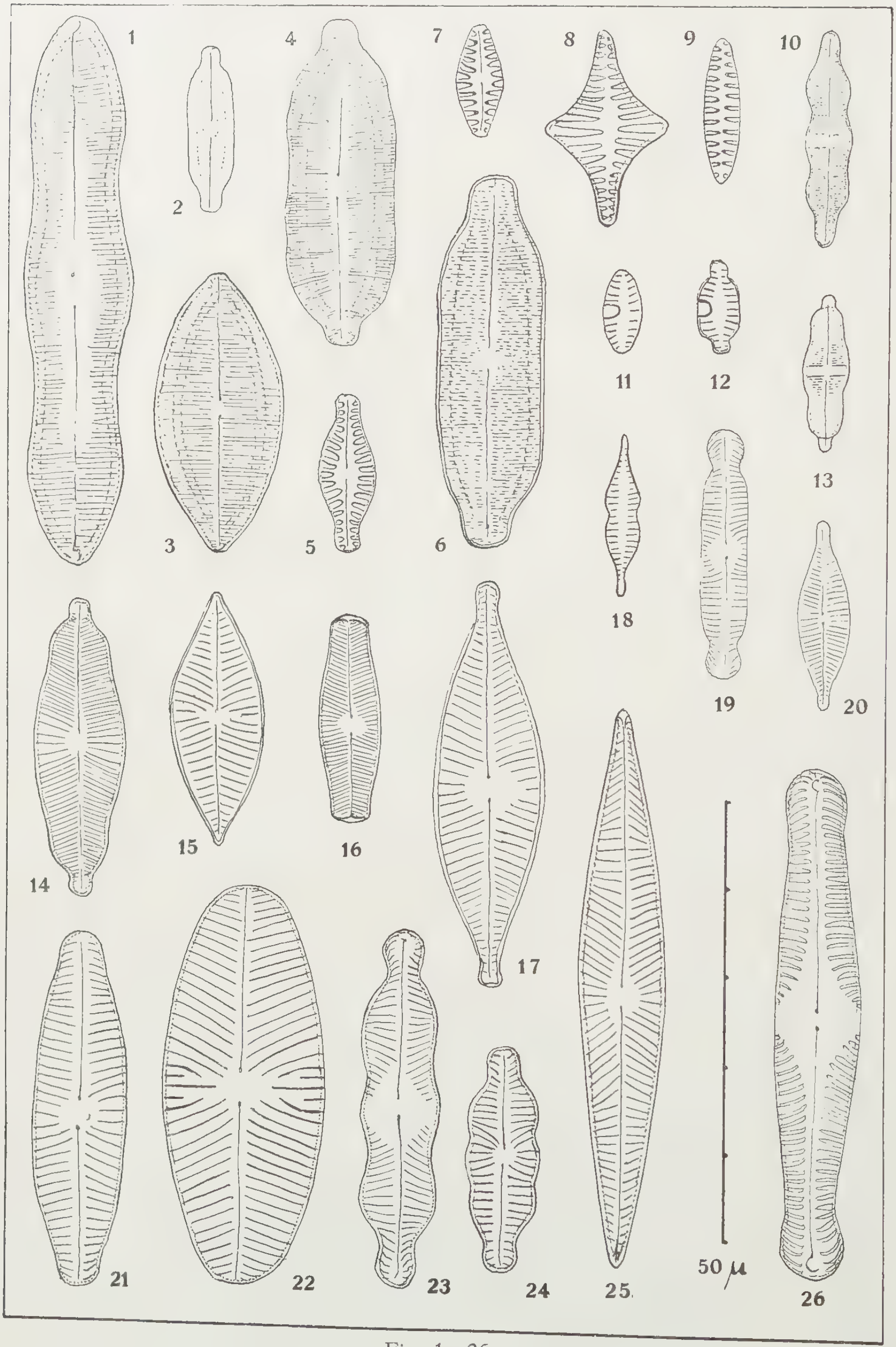

Fig. 1—26.

te voorschijn, n.l. die der halophile en der boreaal-montane soorten. Min of meer halophil zijn o.a.: *Coscinodiscus lacustris, Diploneis*

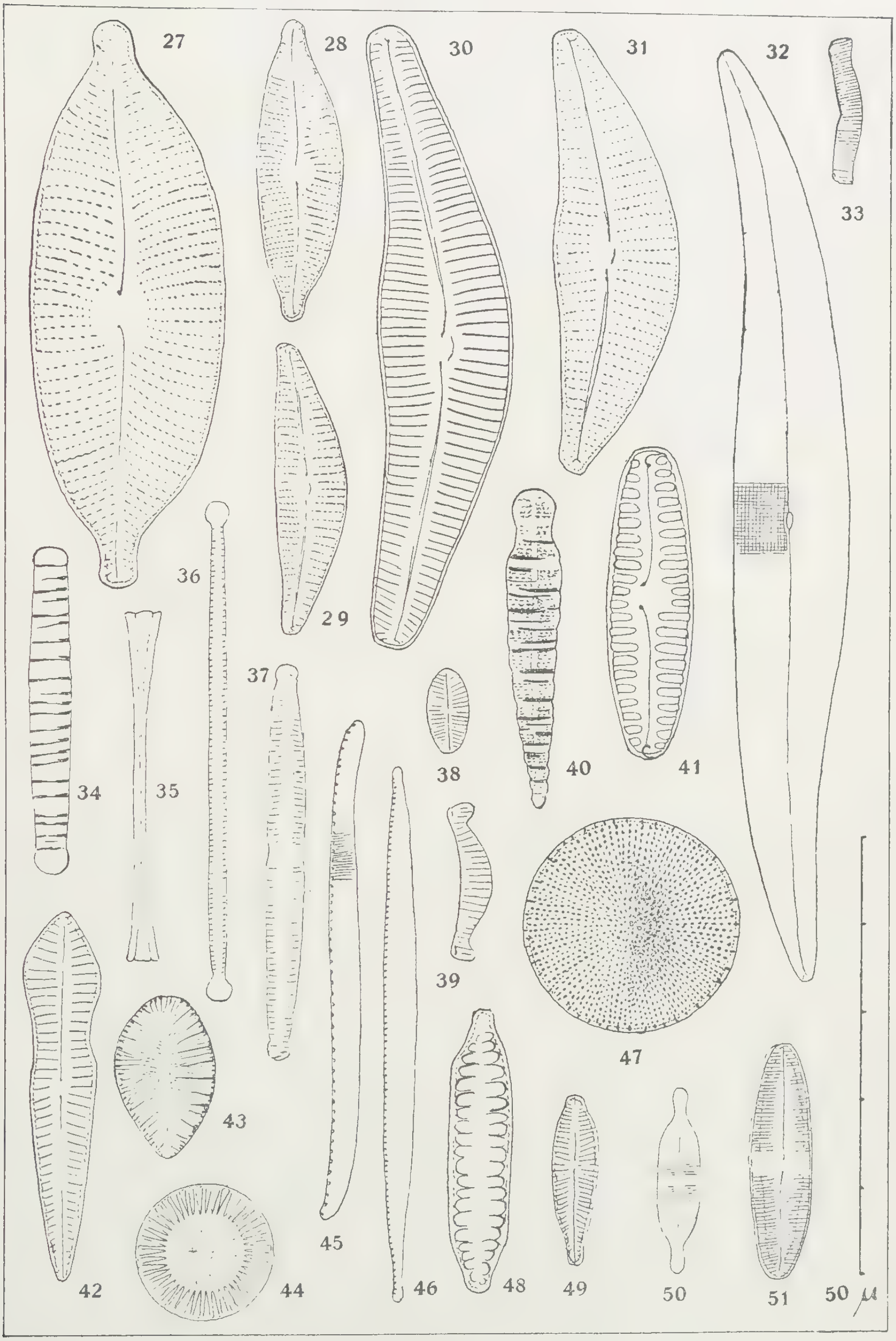

Fig. 27 -51.

interrupta (als zeer kleine vorm van 22 μ lengte, *Mastogloia Brauni, Nitzschia tryblionella, Caloneis amphisbaena* en *Nitzschia scalaris*.

Als noordelijke en gebergtesoorten worden aangerekend: *Pinnularia lata* en *Surirella elegans*. Eerstgenoemde soort is zeer variabel, zoodat ik eerst in twijfel stond of dit niet de hoog-noordelijke soort: *Pinnularia* alpina W. Smith was, maar eenige latere vondsten kwamen beter met *P. lata* overeen, zoodat ik dezen opvallenden vorm (fig. 52) hiertoe heb gebracht.

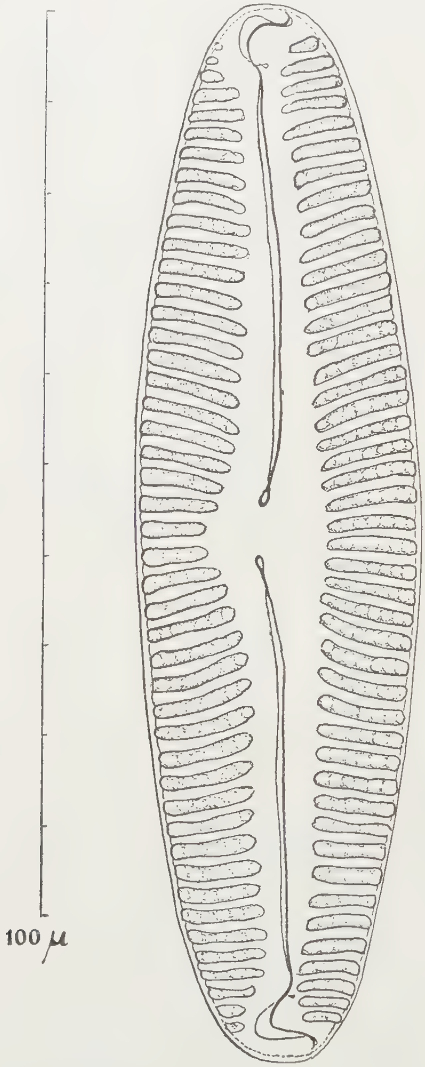

Fig. 52. *Pinnularia lata* (Bréb.) W. Smith ?

FIGURENVERKLARING (FIGURENERKLÄRUNG).

1. Caloneis silicula (Ehr.) Cleve; 2. Neidium affine, v. amphirhynchus (Ehr.) Cleve; 3. Neidium dubium (Ehr.) Cleve, forma ?; 4. Neidium dubium, f. constricta Hust.; 5. Navicula hungarica, v. capitata (Ehr.) Cleve; 6. Neidium dubium (Ehr.) Cleve, fa.; 7. Fragilaria Harrissonii, v. rhomboides Grun.; 8. Fragilaria Harrissonii W. Smith; 9. Fragilaria pinnata Ehr.; 10. Stauroneis legumen Ehr.; 11. Achnanthes lanceolata, v. elliptica Cleve; 12. Idem, v. rostrata Hust.; 13. Stauroneis Smithii Grun.; 14. Navicula integra (W. Smith) Ralfs; 15. Navicula menisculus Schumann; 16. Navicula pupula, v. capitata Hust.; 17. Navicula rhynchocephala Kütz.; 18. Synedra parasitica (W. Smith); 19. Pinnularia interrupta, f. minutissima Hust.; 20. Navicula cryptocephala Kütz.; 21. Navicula viridula, v. slesvicensis (Grun.) Cleve; 22. Navicula gastrum Ehr., fa. 1; 23. Pinnularia mesolepta (Ehr.) W. Smith; 24. Navicula dicephala, v. neglecta (Krasske) Hust.; 25. Navicula radiosa Kütz.; 26. Pinnularia gibba Ehr.; 27. Cymbella cuspidata Kütz.; 28. Cymbella naviculiformis Auerswald; 29. Cymbella turgida (Greg.) Cleve; 30. Cymbella cymbiformis (Agard ? Kütz.) v. Heurck; 31. Cymbella cistula (Hempr.) Grun.; 32. Gyrosigma acuminatum (Kütz.) Rabh.; 33. Eunotia tenella (Grun.) Hust.; 34. Diatoma vulgare Bory; 35—36. Asterionella gracillima (Hantzsch) Heiberg; 37. Fragilaria capucina Desm.; 38. Navicula minima Grun.; 39. Eunotia arcus Ehr.; 40. Meridion circulare, v. constricta (Ralph.) v. Heurck; 41. Pinnularia borealis Ehr.; 42. Gomphonema acuminatum, v. trigonocephala (Ehr.) Grun.; 43. Surirella ovata Kütz.; 44. Cyclotella Meneghiniana Kütz.; 45. Nitzschia ignorata Krasske; 46. Nitzschia subtilis (Kütz.) Grun.; 47. Coscinodiscus lacustris Grun.; 48. Surirella linearis W. Smith; 49. Gomphonema angustatum, v. producta Grun.; 50. Stauroneis parvula Grun. (forma ?); 51. Caloneis bacillum (Grun.) Mereschkovsky; 52. Pinnularia lata (Bréb.) W. Smith.

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1. Roder Diep, bij de brug in den straatweg Roden—Peize, 1. V. 1932.
2. Roder Diep, bij de brug in den straatweg Norg—Donderen, 1. V. 1932.
3. Slokkert, bij de brug in den straatweg Norg—Veenhuizen, 1. V. 1932.
4. Winder Diep, bij de brug in den straatweg Peize—Donderen, 1. V. 1932.
5. Drentsche Aa, bij de brug in den straatweg Vries—de Punt, 3. V. 1928.
6. Looner Diep, bij de brug in den straatweg Assen—Rolde, 20. II. 1939.
7. Rolder Diep, bij de brug in den straatweg Rolde—Gieten, 20. II. 1939.
8. Tjonger, bij de brug in den straatweg Oosterwolde—Veenhuizen, 2. V. 1932.
9. Beiler Stroom, bij de brug in den straatweg Wittelte—Dwingeloo, 24. IV. 1928.
10. Oude arm v. d. Beiler Stroom bij Lheebroek, 16. IX. 1931.
11. Hijker Stroompje, bij de brug in den straatweg Beilen—Hijken, 24. IV. 1928.
12. Ruimsloot, bij de brug in den harden weg Beilen—Westerbork, 14. XII. 1931.
13. De Leek in de Vledder bij Wijster, 7. IX. 1923.
14. Beiler Stroom, bij de brug in den straatweg Westerbork—Elp, 13. XII. 1931.
15. Vledder Aa, bij de brug in den straatweg Frederiksoord—Diever, 26. V. 1932.
16. Vledder Aa, bij de brug in de straat Frederiksoord—Havelte, 26. V. 1932.
17. Ruiner Aa, bij de brug in zandweg Anholt—Kraloo, 19. V. 1932.
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19. Tak Ruiner Aa, bij brug straat Ruinen—Echten, 19. V. 1932.
20. Echtener Stroompje, bij brug weg Hoogeveen—Pesse, 19. V. 1932.
21. Loodiep, nabij den oorsprong bij Meppen, 20. II. 1939.
22. Drostendiep, bij de Klencke, brug in den weg n. Z. Sleen, 2. XII. 1934.
23. Zijtak Drostendiep, bij brug in den weg Emmen—Dalen, 2. XII. 1934.
24. Zijtak Drostendiep, bij brug in den weg Z. Sleen—Emmen, 2. XII. 1934.
25. Zijtak Drostendiep, bij brug in den weg Emmen—N. Sleen, 2. XII. 1934.

Diatomeen aus den Bächen der Provinz Drente (Niederlande).

(Zusammenfassung.)

Die ursprünglichen Wasserläufe des vormaligen Heide- und Hochmoorgebietes der Provinz Drente sind langsam fliessende Bäche, welche im Sommer öfters trocken sind. Sie führen eutrophes, an Humusstoffen reiches Wasser. Das Diatomeenmaterial (Styraxpräparate) 25 verschiedener Fundorte wurde untersucht und das Ergebnis tabellarisch dargestellt. Diese Fundorte wurden auf der Karte und auf der Tabelle übereinstimmend numeriert. Die Nummern I, II, III beziehen sich resp. auf das Abflussgebiet nach dem Wattenmeer, dem IJsselmeer und der Vecht hin. A, B, C u. s. w. stellen die Abflussgebiete der Bäche vor.

Die Diatomeenflora des Gebietes wies, was die Arten betrifft, so ziemlich dieselbe Zusammensetzung und mehrere für das Gebiet typische Formen auf. Ausserdem wurden einige halophile Arten, wie Coscinodiscus lacustris, Diploneis interrupta (sehr kleine Form von 22 μ Länge) Mastogloia Brauni u.a. angetroffen. Bemerkenswert sind auch die boreal-alpinen Arten, wie: Pinnularia lata (mit zu Pinn. alpina neigender Form, siehe Fig. 52) und Surirella elegans. Zur Bestimmung der Arten und Formen wurden hauptsächlich HUSTEDT's Arbeiten: „Bacillariophyta" in PASCHER's Süsswasserflora (1930) und Die „Kieselalgen" in RABENHORST's Kryptogamenflora herangezogen.

Biochemistry. — *Behaviour of microscopic bodies consisting of biocolloid systems and suspended in an aqueous medium.* IV. *Vacuolation phenomena of complex coacervate drops at a constant temperature. Formation of foam structures and of thin-walled drops with a large central vacuole.* By H. G. BUNGENBERG DE JONG and O. BANK. (Communicated by Prof. H. R. KRUYT.)

(Communicated at the meeting of February 25, 1939.)

Introduction.

After mixing a positively charged gelatin sol with a negatively charged gum arabic sol, provided the mixing-ratio and pH are not too unfavourable, we find complex coacervation [1]).

To every mixing-ratio belongs a certain pH at which the coacervation is optimal and at the same time reversal of charge takes place. At a lower pH the coacervate drops have a positive charge, at a higher pH a negative one. The morphology of the vacuolation phenomena described below is different according as we start from a negatively or a positively charged complex coacervate. Data concerning the systems used for this investigation as regards the pH of optimal coacervation and reversal of charge will therefore be given first: We made use of isoelectric gelatin [2]) and of Na-arabinate [3]), viz. a radical solution was prepared from 12 gr. of Na-arabinate + 10 gr. of isoelectric gelatin + 380 cc of distilled water. At 36° each time 5 cc of this mixture was pipetted into a series of tubes of the shape as produced in fig. 1 and then x cc of HCl 0.1 N + $(7{,}5 - x)$ cc of distilled water. After mixing thoroughly, the tubes were hung in a thermostat of 36° and after ± 10 minutes a cohesive coacervate layer was obtained by centrifugation during a short time with a hand-centrifuge. After another 10 minutes in the thermostat, the centrifugation was repeated and the coacervate volumes were read (table, column 2). Only the mixtures

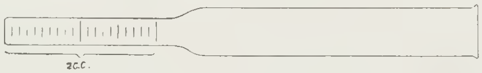

Fig. 1.

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[1]) For elaborate researches on complex coacervation see: H. G. BUNGENBERG DE JONG and W. A. L. DEKKER, Koll. Beihefte, **43**, 143 (1935); **43**, 213 (1936).

[2]) For starting-product and preparation of the isoelectric gelatin see in: H. G. BUNGENBERG DE JONG and W. A. L. DEKKER, Koll. Beihefte, **43**, 213 (1936), see p. 256.

[3]) For the preparation we refer to: H. G. BUNGENBERG DE JONG and P. H. TEUNISSEN, Koll. Beihefte, **47**, 254 (1938).

TABELLE I.

Added cc. HCl 0.1 N (= x)	Coacervate volume (cc.)	pH	U Electrophoretic velocity (arbitrary units)
0.45	0		
0.55	0.39		
0.65	0.96		
0.75	1.22	3 58	— 317
0.90	1.22	3.37	— 122
1.00	1.25	3.18	— 1
1.15	1.19	2.98	+ 113
1.25	1.10	2.89	+ 127
1.40	0.73	2.75	+ 133
1.60	0		

with $x = 0{,}55$ and $0{,}65$ resp. were centrifuged once more after a long time. The read coacervate volumes, recorded in column 2, of these two x values are somewhat too small, the upper layers still being slightly turbid. Of identically composed mixtures, however, with a final volume of 50 cc

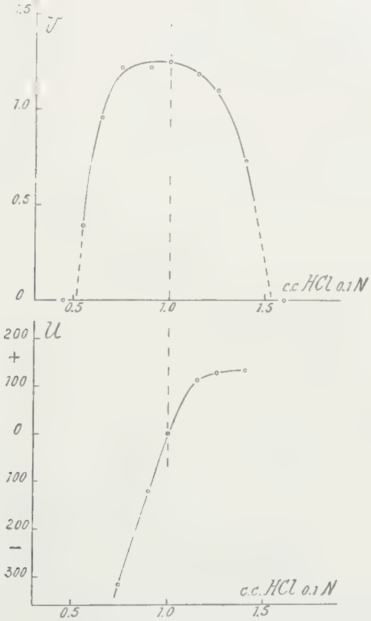

Fig. 2. Connection between optimal coaservation and reversal of charge.
Ordinates: V = volume of the coacervate.
U = electrophoretic velocity in arbitrary units.

instead of 12,5 cc, were yet determined the pH of the systems and the electrophoretic velocity (in arbitrary units), both at 36° [1]).

The results have been collected [2]) in table I.

From fig. 2 may be seen that the optimal coacervation takes places at the reversal of charge.

2. *Formation of coacervate drops with numerous smaller enclosed vacuoles, with foam structure and one large central vacuole resp.*

After the coacervate layers had been completely centrifuged, the centrifugal tubes (see fig. 1) were placed in water of room-temperature, as the result of which the coacervates gelatinize and at the same time a loose flocculated mass separates from the upper layer. This flocculated mass is of its nature likewise a gelatinized complex coacervate [3]).

After half an hour the turbid upper liquid was poured from the now opaque [4]) gelatinized coacervate and the tubes rinsed with distilled water, after which to each tube 12.5 cc of distilled water is added. Subsequently the tubes were placed in the thermostat at 36°. The gelatinized layer of coacervate now becomes again liquid and transparent. After a sufficiently long period (5 to 10 min.) the content of the tubes is carefully shaken. Powerful shaking should be avoided, in order to prevent the molten coacervate from dividing into too small droplets. Now a little of the obtained turbid system is brought on an object-glass and the tube is again placed in the thermostat of 36°. Microscopical examination immediately after placing on the object-glass reveals in all coacervates the presence of vacuolation phenomena. Morphologically, however, we can clearly distinguish two types of these phenomena. According to the table II below, the type of vacuolation is closely connected with the condition of the charge of the original coacervate.

If the coacervate originally was uncharged or had a positive charge, several small vacuoles, lying relatively far apart, occur in the coacervate.

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[1]) It is absolutely necessary to perform the pH and electrophoretic determinations at the same temperature. On cooling of the systems to room-temperature, pH shiftings as well as changes in the electrophoretic velocity occur, accompanying the gelatination of the coacervate drops.

[2]) A specially constructed cuvette was used for the microscopical measurement of the electrophoretic velocity, enabling us to measure at a higher temperature.

[3]) By heating these floccules are again completely dissolved in the upper layer. When they are centrifuged and then heated in a little of the upper layer, typical coacervate drops are formed, which after cooling behave in the same was as the original complex coacervate drops. The amount of separated floccules is a minimum at the reversal of charge. At the same time there is a minimum of arabinate + gelatin present in the upper layer; i.e. the solubility of the coacervate at the reversal of charge is a minimum. By cooling this solubility evidently decreases.

[4]) Opaque, owing to the separation of numerous very small vacuoles. This vacuolation, accompanying the gelatination of the complex coacervates, does not form the subject of this communication.

TABLE II.

cc HCl 0.1 N	Charge	Morphol. appearance of the coacerv. dr. after mixing of molten coacervate with distilled water, after the given number of minutes		
		½	5	10 min.
0.55	− − − −	ring str.	ring str.	ring str.
0.65	− − −	foam str. a. ring str.	,,	,,
0.75	− −	,, ,, ,,	,,	,,
0.90	−	,, ,, ,,	foam str. a. ring	foam str. a. ring
1.00	0	vac. str.	vac. str.	vac.
1.15	+	,, ,,	,, ,,	,,
1.25	++	,, ,,	,, ,,	,,
1.40	+++	,, ,,	,, ,,	,,

Sometimes these vacuoles may yet become fairly large, but they do not flatten each other and consequently retain their globular shape (see fig. 3).

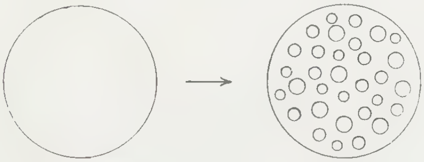

Fig. 3. Vacuolation of the positive coacervate drops.

After five or ten minutes in the thermostat, apart from small alterations in the size of the vacuoles, no change occurs in the morphological appearance of the vacuolated coacervate drops. After a sufficiently long period in the thermostat, the vacuoles disappear (in all probability by passing out) and consequently again exclusively homogeneous coacervate drops are found.

The changes displayed by the originally negative coacervate drops are of quite a different nature. Immediately after the shaking of the molten coacervate layer with the distilled water, miscroscopical examination reveals by the side of other forms discussed below coacervate drops with a foam structure. The often fairly large vacuoles flatten each other and are only separated by thin coacervate lamellae. The foam structure develops here peripherally, which may be excellently observed in large coacervate drops. In order to be able to observe the various stages of foam formation in one and the same preparation side by side, we should in particular examine the coacervates which originally have a weak negative charge, e.g. the coacervate formed with 0.9 cc of HCl 0.1 N. Evidently the source of energy playing a part in the formation of the voluminous vacuoles is fairly soon exhausted here and we observe all the different stages side by side immediately or after 5 or 10 min. In some usually very large coacervate drops we notice then that the foam formation starts in the peripheral layers of the coacervate drop (see fig. 4*a* → *b* → *c*), in other smaller ones the transition into a foam mass has already been completed (see microphotograph *A*).

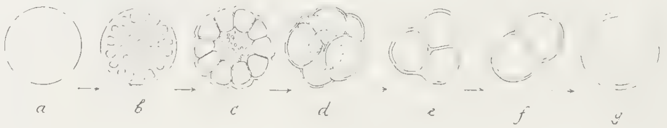

Fig. 4. Formation of the liquid hollow spheres from negative coacervate drops.
a. Initial stage: homogeneous coaiervate drops.
b and c. Peripheral formation of the foam vacuoles. In the centre a granulation may be observed, probably produced by numerous small vacuoles.
d. The whole coacervate drop has changed into a complex of foam vacuoles.
e and f. By bursting of the foam lamellae, forms occur with a small number of foam vacuoles.
g. Final stage: liquid hollow spheres.
The various forms a — g have been drawn in this diagram arbitrarily all of about the same size.

The number of individual vacuoles, separated by coacervate lamellae, may vary greatly. Frequently also forms are observed with a small number, e.g. 4, 3 or 2, while constantly a large number of coacervate drops is found with only a single very large vacuole (see microphotograph *B*).

Upon examination of the preparation under the microscope, no or hardly any modifications of the various forms are observed. However, this is the result of the gelatination of the coacervate lamellae by cooling. At 36°, however, alterations do occur (provided the original coacervate had a sufficient negative charge). After 5 to 10 min. in the thermostat there is usually very little left of the polymorphy of the coacervate drops with foam structure, which is observed immediately after shaking. Now almost exclusively 1) coacervate drops are found with a very large central vacuole (see Table II: "ring structure", according to the form of the optic section, which is observed microscopically). Evidently these liquid hollow spheres (see microphotograph *C*) originate from the above-mentioned coacervate drops with foam structure by successive bursting of the coacervate lamellae in between the vacuoles (see fig. 4*d* → e → *f* → *g*).

3. *Liquid hollow spheres.*

The hollow spheres, formed after a short while from the coacervate drops with foam structure, are in several respects remarkable. In the first place, the relative stability of this structural form. At 36° they remain to exist for a fairly long time (e.g. more than 20 min.), in spite of the fact

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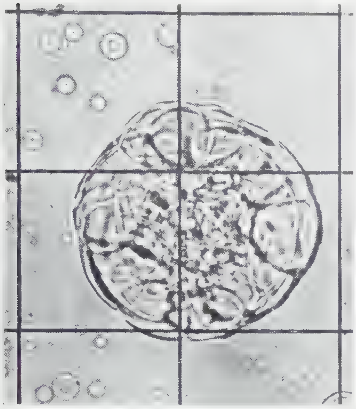
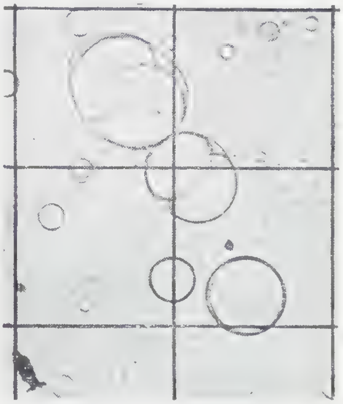
1) By the side of a small fraction of more complex forms, chiefly f of fig. 4.

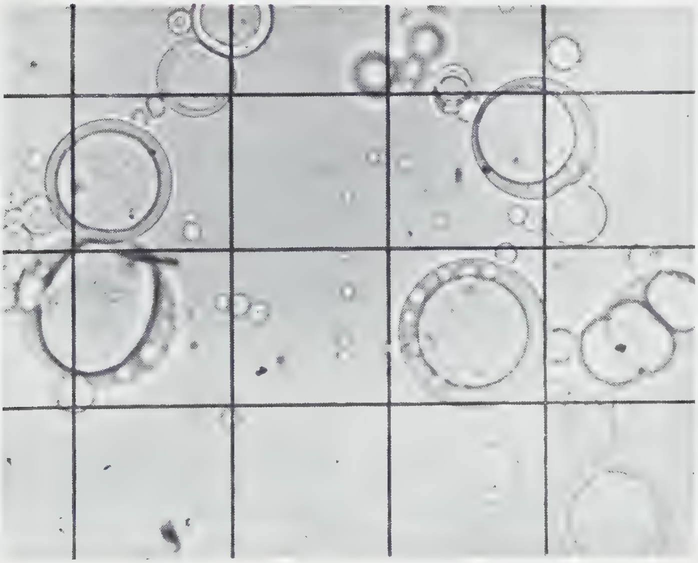
H. G. BUNGENBERG DE JONG AND O. BANK: BEHAVIOUR OF MICROSCOPIC BODIES CONSISTING OF BIOCOLLOID SYSTEMS AND SUSPENDED IN AN AQUEOUS MEDIUM. IV. VACUOLATION PHENOMENA OF COMPLEX COACERVATE DROPS AT A CONSTANT TEMPERATURE. FORMATION OF FOAM STRUCTURES AND OF THIN-WALLED DROPS WITH A LARGE CENTRAL VACUOLE.



A (160 ×)



B (160 ×)



C (160 ×)

Proc. Kon. Ned. Akad. v. Wetensch., Amsterdam, Vol. XLII, 1939.

that the coacervate lamella enclosing the large vacuole is very thin and the internal coacervate lamellae separating the vacuoles in the coacervate drops with foam structure are indeed rapidly destroyed. The outer surface of the hollow sphere may be in a special condition.

In the typically developed hollow spheres (see microphotograph *B*) the volume of the central vacuole is often a multiple of the volume of the globular skin of coacervate enclosing it. Frequently we find that the total diameter and the diameter of the vacuole stand in the relation of 9 : 8, which corresponds with a volume of the vacuole which is 2.4 times larger than that of the coacervate. It is also remarkable that during the beginning of the existence of the hollow spheres the thickness of the wall of the coacervate layer everywhere appears to be equally great. In all probability there is a mechanism which, when the centring of the vacuole threatens to get lost, corrects this again and which is connected with the relative long duration of their existence.

In spite of this, yet the hollow spheres ultimately degenerate, viz. by the decreasing volume of the central vacuole (and perhaps by passing out), so that finally they change into homogeneous coacervate drops 1). The hollow spheres reproduced in microphoto *C* are already in this stage of decrease of the volume of the central vacuole. In the larger specimens this volume is here averagely somewhat smaller than the volume of the globular skin of coacervate (± 0.8). Besides, in some drops we already notice defects with regard to an ideal centring of the vacuole. If now we raise the question for what reason the mentioned decrease in volume of the central vacuole takes place, we should bear in mind that the form of the liquid hollow sphere from the point of view of free boundary surface energy cannot be a stable one. During its formation, by a process which will be discussed below, work has been done against the free boundary surface energy. There is now every reason to assume that this process doing work has not ceased immediately but with a gradually decreasing intensity continues for some time.

Consequently, during the time that the typical hollow spheres exist, we have constantly to deal with two free energies:

A. one trying to press water into the vacuole;

B. the free boundary surface energy, constantly aiming at the smallest possible macro boundary surface of the coacervate and therefore trying to press water from the vacuole.

During the formation of the hollow spheres *A.* prevails entirely, after some time *B.* begins to predominate. In between, consequently, there must

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1) These coacervate drops may be distinguished from the original ones, and also from the coacervate drops formed by dist. water from the original positive coacervate, in this way that at 36° after sedimentation in the tube they can not or only with great difficulty melt into a homogeneous coacervate layer. The supposition suggested above, that the outer surface of the hollow spheres is in a special condition (e.g.gel condition), thus gains in probability.

be a time when the hollow sphere does not change in dimensions, the two processes counterbalancing each other. The hollow sphere then seems to be in equilibrium with its surroundings, although in reality it is in a stationary condition.

Observations.

1. If it were possible to cause the free energy mentioned under A. to remain constant from now onwards or to place it on another constant level, the liquid hollow sphere in the first case would remain unaltered in dimensions, in the secound case it would change into one with other but again constant dimensions.

This seems not devoid of interest with regard to biology. It might be possible that not all cell structures have a static character but some also such a dynamic nature. A change in the functional condition of the cell might then be accompanied by in principle reversible changes of these dynamic structures.

2. The above-described hollow spheres are not specific to the complex coacervate from positive gelatin + negative arabic acid, but were also obtained in other complex coacervates, as far as they are examined in this respect (positive gelatin + negative nucleic acid; positive egg albumin + negative arabic acid), again by sufficient negativation. We may expect, consequently, that we have to deal here with a common characteristic of the complex coacervates. It is hardly doubtful, therefore, that the morphological forms, which W. BERG[1]) observed microscopically already more than thirty years ago in the reaction of protamine solutions (clupeine sulphate) on dried ammonium nucleinate lamellae and which he called „Hohlkörper", likewise belong to the same category.

The description of his experiments does not enable us to get acquainted with all the factors (e.g. of the pH) playing a part in their formation, but yet we may conclude from it that here also a strong negativation first made the formation possible.

The original separated homogeneous unmixing drops with excess of protamine in the solution (read: positively charged complex coacervate drops) were vacuolated and changed into Hohlkörper, if by the existing convection current in the liquid they were driven very close to the nucleinate lamela (read: by absorption of nucleinate in the coacervate reversal of charge and strong negativation set in). W. BERG also observed that already formed Hohlkörper lose their characteristic form and again change into homogeneous drops, if a protamine solution in excess reacts upon them. It should be remarked here that also with the above-described liquid hollow spheres from gelatin and arabinate a positivation (e.g. by addition of a little HC1) makes them rapidly change into homogeneous coacervate drops.

3. Finally it may be observed that the phenomena described here of abnormal enlargement of the vacuoles are not restricted to the complex colloidal systems in the limited sense of the word (consisting of two oppositely charged biocolloids) but may occur as well in autocomplex systems (where the role of one of the biocolloids is taken over by a similarly charged crystalloid ion). In the first communication of this Series[2]), namely, pulsating vacuoles were described in coacervates formed out of gum arabic + basic dyes. Transitory forms occurred there, which here we called liquid hollow spheres, and again under circumstances causing a very strong negativation, viz. when the originally homogeneous coacervate drops were surrounded by the gum arabic solution.

4. *Provisional theory of the vacuolation phenomena.*

In the experiments described above the molten gelatinized coacervate layer was shaken with 12.5 cc of distilled water. If a larger volume of distilled water is taken, also originally uncharged or positive coacervates may produce foam- and ring-structured coacervate drops respectively. Upon 50 cc of distilled water being taken, this is for example the case with the coacervates prepared with 1.00, 1.15 and 1.25 cc of HCl 0.1 N. The striking connection between morphological appearance and original condition of the charge, observed after mixing with a little distilled water, is then no longer present. However, electrophoretic measurements show that the coacervate drops, which are now formed, have a strong negative charge.

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[1]) W. BERG, Archiv. f. Mikrosk. Anat. **65**, 298 (1905).

[2]) H. G. BUNGENBERG DE JONG, Proc. Kon. Ned. Akad. v. Wetensch., Amsterdam, **41**, 643 (1938).

Coacervate drops with a typical "ring structure" may also be obtained from a positive coacervate by a repeated treatment with 12.5 cc of distilled water. After the first treatment vacuolated coacervate drops are formed from the positive coacervate prepared with 1.25 cc of HCl 0.1 N. If now these are centrifuged, the coacervate layer which now is turbid owing to the enclosed vacuoles is left to gelatinize, the upper layer is poured off and 12.5 cc of distilled water are added, we see that, after melting of the gelatinized coacervate layer and shaking at 36°, typical coacervate drops are formed with a large central vacuole.

This experiment also points in the direction that the fact whether foam- and ring-structured coacervate drops are formed is not so much connected with the original sign of the charge of the coacervate as with the question whether the negativation of the coacervate, produced by a raised pH, goes so far that the coacervate drops ultimately possess a strong negative charge.

Further researches, which will be published more extensively elsewhere, show that in the explanation of the vacuolation forms described here we have to distinguish:

a. a primary vacuolation, connected with the washing away of the neutral salt formed during the complex coacervation;

b. possible secondary changes of the formed vacuoles, which are connected with a sufficiently strong negative charge of the coacervate drops.

ad a. The primary vacuolation may be understood from the results of previous researches [1]. It appeared from analyses that addition of a neutral salt in a low concentration causes the water content of the complex coacervate to increase. Withdrawal of a neutral salt from a complex coacervate consequently results in water repulsion = vacuolation. Upon shaking of the coacervate with distilled water indeed withdrawal of a neutral salt takes place, viz. in our case of NaCl, which has been formed during complex coacervation and distributed over the two layers. With certain restrictions, discussed more elaboratly elsewhere [2], complex coacervation may namely be regarded as a double conversion. At optimal coacervation this may be formulated:

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[1] H. G. Bungenberg de Jong and W. A. L. Dekker, Kolloid Beihefte **43**, 213 (1936), see p. 255—261.

[2] H. G. Bungenberg de Jong, Kolloid Z. **80**, 221 (1937).

Gelatin chloride + Na-arabinate → gelatin arabinate. n aq. + NaCl.

In our case we can also calculate roughly how strong is the concentration of the NaCl after coacervation [1]). At the reversal of charge, for example, has been added 1 cc of HCl 0.1 N per 12.5 cc final volume, which yields a concentration of 8 m. aeq. per L. The pH is 3.18, i.e. the H conc. is only 0.66 m.aeq. per L. From this it follows that at the double conversion NaCl is formed of a concentration up to ± 7.3 m.aeq. per L.

If we shake the isolated coacervate layer with a dilute NaCl solution (e.g. 10—15 m.aeq.) instead of distilled water, we obtain only homogeneous coacervate drops. This may be easily understood, since the withdrawal of NaCl from the coacervate, resulting in primary vacuolation, now no longer can take place.

ad b. Above we came already to the conclusion that, when upon shaking of the coacervate drops with distilled water the coacervate obtains a sufficiently strong negative charge, the vacuoles formed by primary vacuolation swell strongly, while the coacervate lamellae separating them grow thin (foam structure) and finally burst (ring structure). Apparently a water transport takes place from outside through the coacervate to the vacuoles. Concerning the mechanism of this water transport we can, in expectation of more extensive researches, only express our opinion with some reserve.

First of all we might be inclined to think of an ordinary osmotic water transport through the coacervate to the vacuole containing a little salt (here NaCl). However, the fact that the formation of hollow spheres is not prevented, if we shake the coacervate layer with cane sugar solutions instead of distilled water (e.g. with a solution of 0.2 mol per L. which certainly is strongly hypertonic with regard to the 7.5 m.aeq. NaCl solution), renders this supposition highly improbable. Moreover, it remains unexplained why in positive coacervates no hollow spheres are formed. For this reason we are inclined to ascribe the water transport towards the vacuoles to an abnormal osmosis.

On account of the importance of the sign of the charge of the coacervate, we think in particular of an electro-endosmotic liquid transport. Here a membrane potential between vacuolar liquid and outer liquid would play a part, in such a way that the first is negative with regard to the second. In case of a negative charge of the coacervate an electro-endosmotic transport from outside inwards would then be the result.

This supposition, which however is suggested with due reserve, is in agreement with the different behaviour of the liquid hollow spheres towards addition of non-electrolytes (e.g. cane sugar) and electrolytes (e.g. salts) in low concentrations. If to an existing system with liquid hollow spheres cane sugar and NaCl respectively are added to a final concentration of 10 millimol per L., in the first case practically no alteration takes place; with NaCl on the other hand the volume of the central vacuole decreases rapidly and they change into homogeneous coacervate drops. It might be supposed that in the latter case a new membrane potential has been introduced against the original one which had alreadly strongly decreased in intensity, owing to which, provided the sign of the charge of the coacervate lamella in between remained the same, the vacuolar liquid is now rapidly electro-endosmotically transported outside.

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[1]) According to recent researches on the distribution of a neutral salt over a coacervate layer and the equilibrial layer, the concentration in the coacervate is about equally strong as in the equilibrial layer.

Elaborate researches on the mechanism of the liquid displacements discussed here are still being made and will be published elsewhere.

Significance for biology.

It might be considered whether the vacuolation phenomena discussed above, which are accompanied by abnormal enlargement and fusion of the vacuoles under formation of liquid hollow spheres, in addition to other (e.g. normal osmotic) processes may be of importance in the formation of the central vacuole of the typical cell of the higher plants. However this question may be answered, it seems to us that the described vacuolation mechanism probably is of importance in the formation of pathological structures in the cytoplasm, particularly in the so-called "schaumige Degeneration". The supposition that the cytoplasm is a negatively charged complex system is in excellent agreement with the fact that it is in alkaline media that this schaumige Degeneration is produced[1]. Alkalization (raising of pH) namely results in a strong negativation of a complex system, which, as we saw in 2. and 4., is exactly what is needed for the formation of foam structure and ring structure. The phenomena discussed here yield models not only for the schaumige Degeneration of not or hardly vacuolated, e.g. animal cells and their possible reversibility, but also for the analogous phenomena in the typical cell of the higher plants, where foam formation occurs in the very thin layer of cytoplasm.

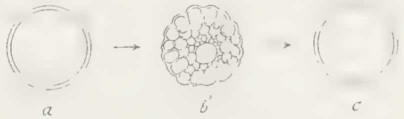

Fig. 5. Influence of a raised pH on liquid hollow spheres.

- a. original condition.
- b. foam formation in the globular skin of coacervate, the original vacuole growing smaller and often incognizable.
- c. Final stage, formed after some time spontaneously from b.

If namely in an already formed system of liquid hollow spheres a further negativation is brought about by careful addition of NaOH, once more foam formation occurs in the globular skin of coacervate (fig. 5, $a \rightarrow b$). The original central vacuole may then shrink considerably and the microscopical image may even be dominated entirely by the new, strongly enlarged vacuoles, formed in the skin of coacervate.

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[1] E. KÜSTER, Pathologie der Pflanzenzelle Teil I, Protoplasma Monographien, Dritter Band, Gebr. Borntraeger, Berlin 1929. See p. 143.

After this system has been left for some time at 36°, the foam structure disappears spontaneously and the typical ring structure is restored (fig. 5, $b \rightarrow c$).

It would lead us too far to enter into details concerning the mechanism of the discussed changes, in particular of the shrinking of the original central vacuole. This will be reserved for a later more extensive publication in Protoplasma.

Laboratory for Medical Chemistry at Leiden.

February 1939.

Biochemistry. — *Behaviour of microscopic bodies consisting of biocolloid systems and suspended in an aqueous medium. V. Gelatinized hollow spheres. Temporary invagination to gastrula-like bodies by mechanical or osmotic removal of water from the central cavity.* By H. G. BUNGENBERG DE JONG and O. BANK. (Communicated by Prof. H. R. KRUYT.)

(Communicated at the meeting of February 25, 1939.)

1. In the preceding communication complex coacervate drops were described with a very large central vacuole (liquid hollow spheres, Hohlkörper). These morphological forms have only a limited stability. It is true that the hollow spheres at 36° remain to exist in the surrounding liquid during at least 20 min., but a real equilibrium is out of the question. The volume of the central vacuole is subject to constant changes. Immediately after the formation of the liquid hollow spheres the volume of the vacuole expands, first rapidly, afterwards more slowly, until after a short stationary condition the volume of the vacuole begins to decrease, first slowly, later more rapidly.

Since during these changes the character of hollow sphere is for the present maintained, they must be accompanied by a constant rearrangement of the liquid particles with regard to each other in the skin of coacervate.

In case of a decrease in volume of the vacuole, for example, the thickness of the skin becomes greater and its two globular surfaces smaller (fig. 1A).

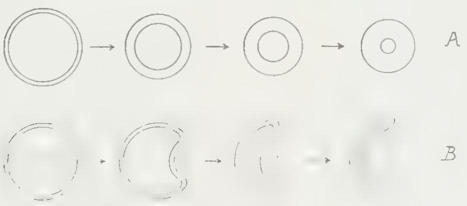

Fig. 1. Removal of liquid from the vacuole in a liquid (A) and a gelatinized (B) hollow sphere. It is supposed that the volume of the coacervate and of the gel during this withdrawal of liquid remains constant.

In this communication we shall discuss a few characteristics of the gel bodies, obtained by cooling of the liquid hollow spheres, in particular the changes they display upon removal of liquid from the central cavity.

Owing to the change of the coacervate into a gel, in these gel bodies rearrangements of the particles with regard to each other, as were possible during the liquid state in the coacervate skin, are not or only to a very slight extent possible in the globular skin of gel which has now been formed.

It is to be expected that, if withdrawal of liquid from the vacuole takes place, the gelatinized skin cannot remain globular. The deformation occurring here is an invagination, unless by forcible means another form of deformation is prescribed (fig. 1B).

This removal of vacuolar liquid may be achieved in two ways:

a. by mechanical means,
b. by an osmotic process.

2. *Invagination after a mechanical pressure and spontaneous reversal of the invagination.*

If a suspension of gelatinized hollow spheres is brought on an object-glass and covered with a cover-glass, it is already sufficient to turn the tube of the microscope down, so that the objective presses against the cover-glass, and to make this pressure last for some seconds to observe invagination in many hollow spheres after the tube has been turned up. After the preparation has been left for some time, it appears that the invagination gradually decreases and finally vanishes completely, the original form of the hollow sphere being restored. We can also put a pressure upon the cover-glass in another way and at the same time continue the examination under the microscope. We find then that the invagination does not set in during the pressure but after this has been removed. Then it takes place suddenly.

In order to be able to explain this (see fig. 2), we have to take into consideration that the gelatinized hollow spheres are elastic. During the pressure, while water is pressed from the vacuole ($B \rightarrow C$), an elastic deformation of the hollow sphere is brought about, invagination not yet playing a part. After the pressure has been removed, the ring body tries to recover its original shape, but this is impossible, the content of the vacuole now being smaller. However, the deformation produced under

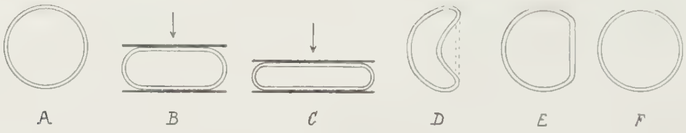

Fig. 2. Reversible invagination by mechanical pressure.
A. original condition.
B and C. deformation between two planoparallel plates.
In B, immediately after application of the pressure, the volume of the vacuole is still equally large as in A; in C, after continued pressure, a considerable amount of liquid has been pressed out.
D. after the pressure has been removed, deformation C changes into an invagination.
E. stage during the spontaneous reversal of the invagination.
F. final stage.

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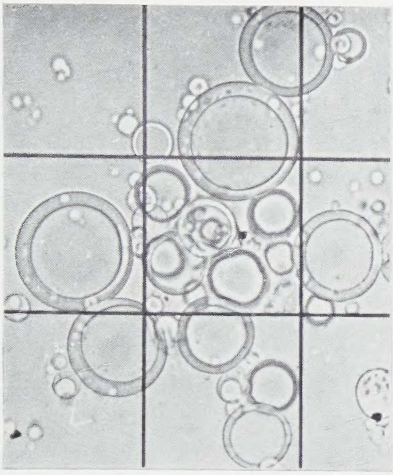

A (160 ×)

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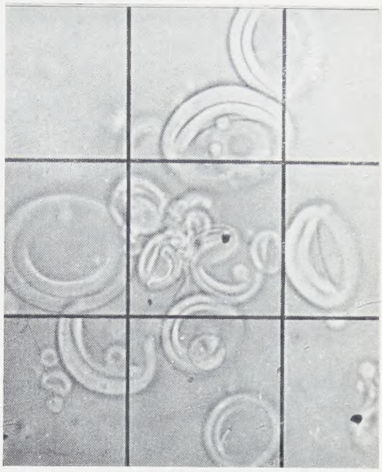

B (160 ×)

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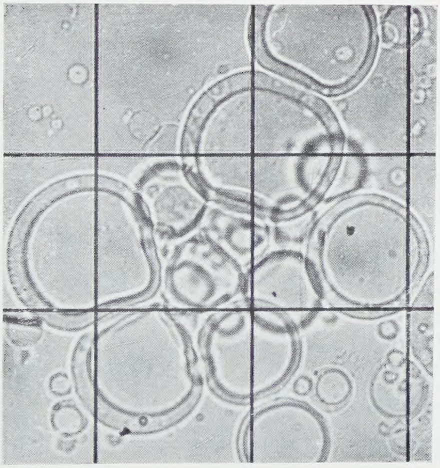

D (160 ×)

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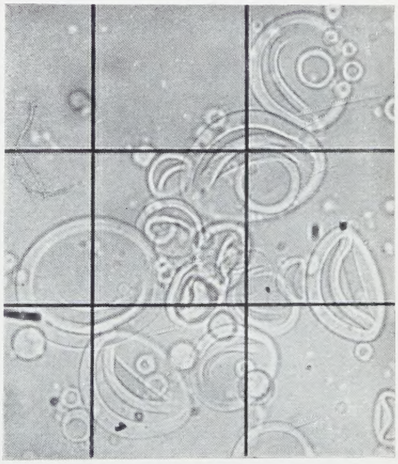

C (160 ×)

Proc. Kon. Ned. Akad. v. Wetensch., Amsterdam, Vol. XLII, 1939.

pressure may spontaneously change into another deformation with the same volume of the vacuole, if this required less deformation energy for its formation starting from the hollow sphere. This deformation is the one where folding (invagination) of part of the globular skin has taken place. In this new condition *D* the elastic stretching, existing in *C* in the upper and lower half of the globular skin, has disappeared and the length of the zone with a strong curvature is considerably smaller.

The condition now obtained (*D*) is still one where an elastic deformation exists and consequently should not be stable. From now onwards, under the influence of the existing elastic deformation, liquid must flow from outside into the vacuole, thus enabling the elastic deformation to decrease. This is indeed the case. Gradually the folding is growing less deep and finally we notice that it disappears completely, the original form being restored (fig. 2*F*). The last rounding ($E \rightarrow F$) usually takes place with surprising rapidity.

3. *Osmotic behaviour of the gelatinized hollow spheres.*

If we bring a suspension of the gelatinized hollow spheres on an object-glass and leave this for some time, they stick to the glass surface, so that upon addition of a drop of aqueous solution most of them remain in their places. The subjoined microphotographs (distance between 2 black lines = 130 μ) refer to the influence of cane-sugar. A photograph was taken of part of the preparation without cover-glass (*A*), then a drop of 30 % cane-sugar solution was carefully placed on it and a second photograph was taken (*B*). We see that a very strong invagination has set in. Twenty minutes afterwards once more a photograph was taken (*C*). Evidently the intensity of the invagination has distinctly decreased. In the large objects the distance between the convex and concave part of the globular skin is distinctly larger, while some small objects, invaginated in *B*, in *C* have become round again.

The described changes may be regarded as the result of a temporary osmotic withdrawal of water from the central cavity, owing to the fact that the permeability of the wall for water is evidently considerably greater than for sugar. After the invagination has set in, no osmotic equilibrium is attained, since cane-sugar also diffuses slowly inwards. Consequently the intensity of invagination decreases gradually.

This spontaneous reversal of the invagination ultimately leads to a complete restoration to the original blastula form. Since in the case of cane-sugar in large objects this process may take a long time, it was accelerated by addition of a fairly large quantity of distilled water (*D*). We now observe yet another phenomenon, viz. that after neutralization of the invagination the hollow spheres now are larger and the globular gel skins thicker than at the beginning of the experiment.

Owing to the fact that the pH was not held constant, this general increase in size may be attributed mainly to a swelling of the gel skin as a result of an increase of pH of the medium (the intensity of the complex relations between positive gelatin and negative gum arabic decreases).

The phenomena discussed above may be realized not only with cane-sugar but also with solutions of other substances, with non-electrolytes as well as with electrolytes. Here distinct differences occur in the time after which, by spontaneous reversal of the invagination, complete rounding is again recovered.

Although quantitative experiments have not yet been made, we are inclined to conclude from qualitative experiments that the permeability of the globular gel skin increases in the order

$$\text{cane-sugar} < \text{glycerin} < \text{alcohol.}$$

With urea invagination may be obtained as well, but now the images are difficult to see and secondary changes are apt to occur, owing to the fact that in this medium the gelatination decreases or is neutralized. As a rule the duration of the invagination produced with salt solutions is only short. This striking difference between salts (e.g. NaCl) and non-electrolytes (cane-sugar, etc.) may for the rest be explained by the secondary reactions by which the former do, the latter do not affect the complex gel of which the globular gel skin consists. Salts, namely, reduce the intensity of the complex relations between positive gelatin and negative gum arabic (in analogy with the neutralizing action of salts on the complex coacervates). The result of the salt reaction is an increasing water content of the complex gel, which makes it conceivable that the permeability of the globular gel skin for salts is much more considerable than for non-electrolytes.

Laboratory for Medical Chemistry at Leiden.

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